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Copper(I)-induced activation of monosubstituted acetylenes. Perturbation of ligand geometry resulting from π-complexation

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Abstract

Three complexes between monosubstituted acetylenes, viz. phenylacetylene, propargyl chloride and propargyl alcohol, and copper(I) chloride have been prepared by direct reaction between copper(I) chloride and the relevant acetylenes. Changes in ligand geometry ensuing from π complexation to copper(I) have been investigated by infrared spectroscopy and crystal structure determinations. In all three compounds copper(I) exhibits trigonal pyramidal coordination geometry with a long apical Cu–Cl bond, the trigonal plane being composed of the midpoint of π-acetylenic linkage and two chloride ligands. The Cu–C bond lengths are 1.999(4) and 2.066(3) Å in $[CuCl(HC{\equiv}CC_6H_5)]$ (**1**), 2.004(3) and 2.004(4) Å in $[CuCl(HC{\equiv}CCH_2Cl)]$ (**2**) and 2.006(10) and 2.018(9) Å in $[CuCl(HC{\equiv}CCH_2OH)]$ (**3**). The C≡C bond is lengthened only slightly on coordination, although ν(C≡C) is lowered by 133, 144 and 154 cm^{-1} for **1**, **2** and **3**, respectively, and there is moderate bending back of the H–C≡C and R–C≡C angles, indicating a relatively weak copper(I)–alkyne interaction. $\nu(C_{sp}{-}H)$ is lowered by 120, 83 and 110 cm^{-1}, relative to the values for the free ligands, in **1**–**3**, respectively. Although this suggests activation of the C_{sp}–H bonds, this is not supported by unusual structural features involving the acetylenic hydrogen atoms.

Key words: Copper; Alkyne; Crystal structure

1. Introduction

Copper(I) π-coordination to terminal alkynes has been shown to activate the C_{sp}–H bond [1]. Although several π complexes between alkynes and copper(I) have been characterised by crystal structure determinations [2–17], few of these studies were concerned with acetylene [4,5] or terminal alkynes [15,16]. Thus structural information concerning perturbation of the H–C≡C fragment and the possible existence of Cu · · · H interactions is relatively scarce.

Previously, we have investigated the coordination geometry of the metal centre and changes in ligand geometry on π-complexation between conjugated [18,19] or non-conjugated [15,20,21] dienes and copper(I) chloride or bromide. Most often, copper(I) exhibits trigonal pyramidal coordination in which the trigonal plane is composed of the midpoint of the C=C linkage and two halogenide ligands and the apical position by a halogenide ligand remote (*ca.* 3 Å) from the copper(I) centre. For tetranuclear π-olefinic complexes with a cubane-type Cu_4X_4 (X = Cl and/or Br) core, it has been possible to show that the observed distortions of the cubane core, resulting from the trigonal pyramidal geometry exhibited by copper(I), are a consequence of the π-acceptor properties of the olefin [21]. A similar coordination geometry has been found for the metal in the complex between copper(I) chloride and 1,7-octadiyne [15]. In addition, there appears to be a relationship between the coordination geometry at the copper(I) centre and the mode of twisting of the coordinated olefin or acetylene out of the trigonal plane [18,19]. We were therefore interested in extending our studies on complexes with copper(I) chloride to include simple monosubstituted alkynes, RC≡CH, primarily to seek evidence for C_{sp}–H activation in the

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solid state, but also to investigate the importance of the R group in inducing structural changes reflecting the nature of the bonding of the C≡C–H fragment to copper(I).

2. Experimental details

All operations were carried out under nitrogen or argon by standard Schlenk or special low-temperature techniques [22]. Phenylacetylene (ethynylbenzene), propargyl chloride (3-chloro-1-propyne) and propargyl alcohol (2-propyn-1-ol) were deoxygenated by freeze–pump–thaw cycles, but otherwise used without further purification. Copper(I) chloride was purified as described in ref. 23 and dried *in vacuo*.

2.1. Preparation of $[CuCl(HC\equiv CC_6H_5)]$ *(1)*

Approximately 0.1 g of copper(I) chloride was mixed with 2 ml of phenylacetylene at room temperature, partial dissolution of the copper(I) chloride yielding a yellow solution. On gentle heating of the mixture, copper(I) chloride dissolved, and a small amount of a bright yellow, flocculant precipitate (presumably copper(I) acetylide) separated. Addition of concentrated hydrochloric acid (*ca.* 0.03 ml) yielded a clear yellow solution. This solution was allowed to cool slowly to ambient temperature, colourless plates of **1** being deposited from the solution after a few days. Crystals of **1** are fairly stable, decomposing only after a few hours' exposure to the atmosphere.

2.2. Preparation of $[CuCl(HC\equiv CCH_2Cl)]$ *(2)*

The compound was prepared by the method used for **1** but starting from 0.1 g of copper(I) chloride and 2 ml of propargyl chloride. Addition of *ca.* 0.15 ml of concentrated hydrochloric acid was required to convert the brownish-yellow colloidal solution obtained on heating of the mixture into a clear orange-yellow solution. This solution was allowed to cool slowly to room temperature and pale-yellow rod-shaped crystals of **2** separated overnight. Crystals of **2** decompose within a few minutes on exposure to the atmosphere at ambient temperature.

2.3. Preparation of $[CuCl(HC\equiv CCH_2OH)]$ *(3)*

The complex $[CuCl(HC\equiv CCH_2OH)]$ (**3**) was prepared by the method used for **1** and **2** but starting from 0.1 g of copper(I) chloride and 2 ml of propargyl alcohol, a clear yellow solution being obtained on addition of *ca.* 0.03 ml concentrated hydrochloric acid. The solution was held at *ca.* 50°C for 1–2 h; it was then allowed to cool slowly to ambient temperature and colourless plates of 3 separated overnight. Crystals of **3** decompose within a few minutes on exposure to the atmosphere at ambient temperature.

2.4. Infrared spectrometry

Measurements were performed on crystalline samples of **1**, **2** and **3**, mixed with Fluorolube® and placed between CaF_2 discs, using a Perkin Elmer 1830 double beam FTIR spectrometer. NaCl discs were employed for the ligand solvents (phenylacetylene, propargyl chloride and propargyl alcohol). Spectra were recorded with a resolution of 2 cm^{-1}. $[CuCl(HC\equiv CC_6H_5)]$ (**1**): $\nu(C_{sp}–H)$ 3172 cm^{-1}, $\nu(C\equiv C)$ 1977 cm^{-1}. Corresponding values for phenylacetylene: 3292 and 2110 cm^{-1}, respectively. $[CuCl(HC\equiv CCH_2Cl)]$ (**2**): $\nu(C_{sp}–H)$ 3216 cm^{-1}, $\nu(C\equiv C)$ 1987 cm^{-1}. Corresponding values for propargyl chloride: 3299 and 2131 cm^{-1}, respectively. $[CuCl(HC\equiv CCH_2OH)]$ (**3**): $\nu(C_{sp}–H)$ 3185 cm^{-1}, $\nu(C\equiv C)$ 1967 cm^{-1}. Corresponding values for propargyl alcohol: 3295 cm^{-1} and 2121 cm^{-1}, respectively.

The infrared absorption frequencies for the complex between phenylacetylene and copper(I) chloride are in good agreement with those reported previously [24], as are those for the free acetylenes [24,25].

2.5. X-ray crystallography

Crystal and experimental data are summarized in Table 1. Crystals of **1**–**3** were mounted in glass capillar-

TABLE 1. Crystallographic data for $[CuCl(HC\equiv CC_6H_5)]$ (**1**), $[CuCl(HC\equiv CCH_2Cl)]$ (**2**) and $[CuCl(HC\equiv CCH_2OH)]$ (**3**)

	1	**2**	**3**
Formula	C_8H_6ClCu	$C_3H_3Cl_2Cu$	C_3H_4ClCuO
M_r	201.1	173.5	155.1
Cryst. system	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_1/c$	$P2_12_12_1$
a(Å)	30.521(3)	10.679(1)	22.311(3)
b(Å)	6.602(3)	3.973(2)	5.132(2)
c(Å)	7.366(3)	13.382(1)	4.099(4)
β(°)	92.77(2)	112.861(7)	90
V(Å^3)	1482.5(9)	523.1(2)	469.4(5)
Z	8	4	4
F(000)	800	336	304
D_c(g cm^{-3})	1.80	2.20	2.19
μ(Mo K_α (cm^{-1})	32.3	50.5	50.8
Temp (°C)	−120	−125	−120
Abs. corr.	Empirical	Empirical	Empirical
Trans. coeff.	0.67–1.00	0.95–1.00	0.76–1.00
$2\theta_{max}$(°)	50	50	50
No. unique refls	1429	1067	541
No. obs. refls.	1054	796	432
No. par. ref.	115	67	59
R	0.026	0.022	0.033
R_w	0.031	0.032	0.046

ies under argon at −150°C [22] and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured using graphite-monochromated Mo Kα ($\lambda = 0.71069$ 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 to 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 showed no significant variations.

For **1**, data were measured for $3.5 < 2\theta < 50°$ from a colourless plate of approximate dimensions $0.30 \times 0.20 \times 0.05$ mm^3, with an ω scan rate of 32° min^{-1} and a scan width of $(1.52 + 0.30 \tan\theta)°$. Correction was made for Lorentz and polarization effects; an empirical correction based on azimuthal scans for several reflections was made for the effects of absorption (minimum/maximum transmission factors = 0.67/1.00). Of the 1429 unique reflections measured ($+h$, $+k$, $\pm l$), 1054 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 $48.4 < 2\theta < 49.9°$. The structure was solved by direct methods (MITHRIL [26]). Full-matrix least-squares refinement, including anisotropic thermal parameters for the non-hydrogen atoms and isotropic for the hydrogen atoms gave a final $R = 0.026$ ($R_w = 0.031$) for 115 parameters and 1054 reflections. The maximum and minimum values in the final difference map were 0.36 and −0.35 e Å^{-3}, respectively. Reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$.

For **2**, data were measured for $3.5 < 2\theta < 50°$ from a pale-yellow rod-shaped crystal with approximate dimensions $0.20 \times 0.20 \times 0.40$ mm^3, with an ω scan rate of 32° min^{-1} and a scan width of $(1.52 + 0.30 \tan\theta)°$. Correction was made for Lorentz and polarization effects; an empirical correction for the effects of absorption was made as for **1** (minimum/maximum transmission factors = 0.95/1.00). Of the 1067 unique reflections measured ($+h$, $+k$, $\pm l$), 796 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 $49.0 < 2\theta < 49.6°$. The structure was solved by direct methods (MITHRIL [26]). Full-matrix least-squares refinement as for **1** gave a final $R = 0.022$ ($R_w = 0.032$) for 67 parameters and 796 reflections. The maximum and minimum values in the final difference map were 0.34 and −0.50 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 colourless plate with approximate dimensions $0.30 \times 0.20 \times 0.05$ mm^3, with an ω scan rate of 32° min^{-1} and a scan width of $(1.31 + 0.30 \tan\theta)°$. Correction was made for Lorentz and polarization effects; an empirical correction was made for the effects of absorption (*cf.* **1** and **2**; minimum/maximum transmission factors = 0.76/1.00). Of the 541 unique reflections measured ($+h$, $+k$, $+l$), 432 had $I > 3.0\sigma(I)$ and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 24 reflections in the range $34.5 < 2\theta < 49.1°$. The structure was solved by direct methods (MITHRIL [26]). The hydrogen atoms bonded to C(3) were included in calculated positions (C–H = 0.95 Å; $B = B_{eq}$ for C(3)) and that bonded to C(1) was located from a difference map, but the hydroxyl hydrogen could not be located with certainty. Full-matrix least-squares refinement, including anisotropic thermal parameters for the non-hydrogen atoms and isotropic for the hydrogen atom bonded to C(1) gave a final $R = 0.033$ ($R_w = 0.046$) for 59 parameters and 432 reflections. The maximum and minimum values in the final difference map were 0.51 and −0.88 e Å^{-3}, respectively. Reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$. The enantiomorph refined to $R = 0.042$ ($R_w = 0.054$).

All calculations were carried out with the TEXSAN [27] program package. Atomic scattering factors and anomalous dispersion correction factors were taken from ref. 28. Structural illustrations have been drawn with ORTEP [29]. Final positional parameters are listed in Tables 2–4 and selected interatomic distances and

TABLE 2. Positional parameters and equivalent isotropic thermal (non-hydrogen atoms) or isotropic thermal parameters (hydrogen atoms) (Å^2) for [CuCl(HC≡CC$_6$H$_5$)] (**1**) [a]

Atom	x	y	z	B_{eq} [b]/B
Cu	0.71797(1)	0.06405(7)	0.14418(6)	1.62(2)
Cl	0.77272(3)	−0.0979(1)	0.3120(1)	1.48(3)
C(1)	0.6775(1)	−0.1514(6)	0.0446(5)	1.7(1)
C(2)	0.6569(1)	0.0045(5)	0.0222(4)	1.4(1)
C(3)	0.6218(1)	0.1482(5)	−0.0159(4)	1.4(1)
C(4)	0.6300(1)	0.3376(6)	−0.0903(4)	1.7(1)
C(5)	0.5957(1)	0.4680(6)	−0.1311(5)	2.1(2)
C(6)	0.5532(1)	0.4114(7)	−0.0986(5)	2.5(2)
C(7)	0.5451(1)	0.2247(7)	−0.0241(6)	2.8(2)
C(8)	0.5790(1)	0.0920(6)	0.0185(5)	2.2(2)
H(1)	0.689(1)	−0.262(6)	0.037(6)	2.8(8)
H(4)	0.658(1)	0.374(6)	−0.110(5)	1.6(7)
H(5)	0.602(1)	0.589(6)	−0.175(5)	1.7(7)
H(6)	0.531(1)	0.501(5)	−0.123(5)	1.7(7)
H(7)	0.517(1)	0.184(6)	−0.010(5)	2.4(9)
H(8)	0.575(1)	−0.046(6)	0.070(5)	2.3(8)

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

TABLE 3. Positional parameters and equivalent isotropic thermal (non-hydrogen atoms) or isotropic thermal parameters (hydrogen atoms) (Å^2) for [CuCl(HC≡CCH$_2$Cl)] (**2**) [a]

Atom	x	y	z	B_{eq} [b]$/B$
Cu	0.12838(4)	−0.0242(1)	0.31437(3)	1.48(2)
Cl(1)	−0.07137(8)	−0.1667(2)	0.32820(6)	1.60(3)
Cl(2)	0.39440(9)	−0.5067(2)	0.64290(7)	2.09(3)
C(1)	0.3299(4)	−0.0530(10)	0.3968(3)	1.9(1)
C(2)	0.2767(3)	−0.1873(9)	0.4509(3)	1.5(1)
C(3)	0.2436(3)	−0.3564(9)	0.5359(3)	1.6(1)
H(1)	0.384(5)	0.033(14)	0.373(5)	6(1)
H(3a)	0.175(4)	−0.545(11)	0.505(3)	3(1)
H(3b)	0.195(4)	−0.186(12)	−0.568(3)	3(1)

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

TABLE 4. Positional parameters and equivalent isotropic thermal (non-hydrogen atoms) or isotropic thermal parameters (hydrogen atoms) (Å^2) for [CuCl(HC≡CCH$_2$OH)] (**3**) [a]

Atom	x	y	z	B_{eq} [b]$/B$
Cu	0.05202(5)	0.8147(2)	0.1207(3)	1.60(5)
Cl	−0.0385(1)	0.9944(5)	0.0098(7)	1.6(1)
C(1)	0.1171(4)	1.037(2)	−0.069(3)	1.7(5)
C(2)	0.1414(4)	0.866(2)	0.081(2)	1.2(4)
C(3)	0.1882(4)	0.699(2)	0.231(3)	1.6(4)
O	0.2456(3)	0.824(1)	0.229(2)	2.0(3)
H(1)	0.108(5)	1.14(2)	−0.19(3)	2(3)
H(3a)	0.191	0.539	0.114	1.9
H(3b)	0.177	0.662	0.452	1.9

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

TABLE 5. Bond distances (Å) and selected angles (°) for [CuCl(HC≡CC$_6$H$_5$] (**1**). X is the midpoint of the C(1)–C(2) bond. Symmetry code: (i): $3/2-x$, $1/2+y$, $1/2-z$; (ii): x, $-y$, $z-1/2$

Cu-C(1)	1.999(4)	C(5)-C(6)	1.383(6)
Cu-C(2)	2.066(3)	C(6)-C(7)	1.377(6)
Cu-X	1.941	C(7)-C(8)	1.381(6)
Cu-Cl	2.295(1)	C(8)-C(3)	1.394(5)
Cu-Cl^{i}	2.271(1)	C(1)-H(1)	0.82(4)
Cu-Cl^{ii}	3.037(1)	C(4)-H(4)	0.90(4)
C(1)-C(2)	1.213(5)	C(5)-H(5)	0.88(4)
C(2)-C(3)	1.449(5)	C(6)-H(6)	0.92(4)
C(3)-C(4)	1.393(5)	C(7)-H(7)	0.90(4)
C(4)-C(5)	1.377(5)	C(8)-H(8)	1.00(4)
Cu···H(1)	2.44(4)		
Cl-Cu-Cl^{i}	107.37(3)	C(2)-C(3)-C(8)	118.8(3)
Cl-Cu-Cl^{ii}	93.07(4)	C(8)-C(3)-C(4)	119.9(3)
Cl-Cu-X	123.67	C(3)-C(4)-C(5)	119.9(4)
Cl^{i}-Cu-Cl^{ii}	88.41(3)	C(4)-C(5)-C(6)	120.2(4)
Cl^{i}-Cu-X	127.67	C(5)-C(6)-C(7)	120.0(4)
Cl^{ii}-Cu-X	98.91	C(6)-C(7)-C(8)	120.7(4)
C(1)-C(2)-C(3)	162.9(3)	C(3)-C(8)-C(7)	119.3(4)
C(2)-C(3)-C(4)	121.3(3)	H(1)-C(1)-C(2)	168 (3)

TABLE 6. Bond distances (Å) and selected angles (°) for [CuCl(HC≡CCH$_2$Cl)] (**2**). X is the midpoint of the C(1)–C(2) bond. Symmetry code: (iii): $-x$, $1/2+y$, $1/2-z$; (iv): $-x$, $y-1/2$, $1/2-z$

Cu-C(1)	2.004(4)	C(1)-C(2)	1.204(5)
Cu-C(2)	2.004(3)	C(2)-C(3)	1.477(5)
Cu-X	1.912	C(3)-Cl(2)	1.792(3)
Cu-Cl(1)	2.283(1)	C(1)-H(1)	0.84(6)
Cu-Cl(1^{iii})	2.264(1)	C(3)-H(3a)	1.01(4)
Cu-Cl(1^{iv})	3.102(1)	C(3)-H(3b)	1.04(4)
Cu···H(1)	2.54(5)		
Cl(1)-Cu-Cl(1^{iii})	105.67(3)	Cl(1^{iv})-Cu-X	101.95
Cl(1)-Cu-Cl(1^{iv})	83.09(3)	C(1)-C(2)-C(3)	166.9(3)
Cl(1)-Cu-X	123.65	C(2)-C(3)-Cl(2)	111.0(2)
Cl(1^{iii})-Cu-Cl(1^{iv})	94.22(4)	H(1)-C(1)-C(2)	166(4)
Cl(1^{iii})-Cu-X	129.32		

angles in Tables 5–7. Tables of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

All three complexes are polymeric and insoluble in common organic solvents, precluding recrystallization of the amorphous products obtained by direct reaction of the relevant components at ambient temperature. Crystals were therefore obtained in a manner analogous to that described previously [15] in which **1**–**3** were brought into solution by heating the reactants to just below the boiling point of the ligand solvent and then allowing the solution to cool slowly to ambient temperature. Formation of copper(I) acetylide was suppressed effectively by the addition of a small amount of concentrated hydrochloric acid.

In all three complexes, copper(I) exhibits the trigonal pyramidal coordination geometry which is now a common feature in *e.g.* complexes between copper(I) chloride and, *e.g.* dienes or diynes [15,18–21]. Thus the

TABLE 7. Selected interatomic distances (Å) and angles (°) for [CuCl(HC≡CCH$_2$OH)] (**3**). X is the midpoint of the C(1)–C(2) bond. Symmetry code: (v): $-x$, $y-1/2$, $1/2-z$; (vi): $-x$, $y-1/2$, $-z-1/2$; (vii): $1/2-x$, $2-y$, $1/2+z$; (viii): $1/2-x$, $2-y$, $z-1/2$

Cu-C(1)	2.006(10)	C(1)-C(2)	1.20(1)
Cu-C(2)	2.018(9)	C(2)-C(3)	1.48(1)
Cu-X	1.919	C(3)-O	1.43(1)
Cu-Cl	2.265(2)	C(1)-H(1)	0.8(1)
Cu-Cl^{v}	2.255(3)	O···O^{vii,viii}	2.741(9)
Cu-Cl^{vi}	3.078(4)	Cu···H(1)	2.4(1)
Cl-Cu-Cl^{v}	108.18(8)	Cl^{vi}-Cu-X	94.5
Cl-Cu-Cl^{vi}	87.79(7)	C(1)-C(2)-C(3)	162(1)
Cl-Cu-X	127.0	C(2)-C(3)-O	111.7(8)
Cl^{v}-Cu-Cl^{vi}	99.30(11)	H(1)-C(1)-C(2)	168(9)
Cl^{v}-Cu-X	123.4		

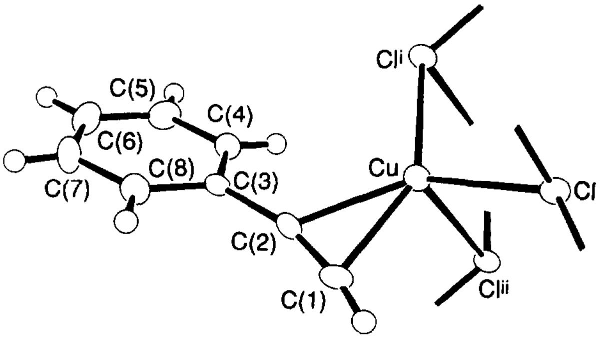

Fig. 1. Part of the layer of $[CuCl(HC\equiv CC_6H_5)]$, **1**, showing the crystallographic numbering. For symmetry code, see Table 5. Thermal ellipsoids enclose 50% probability.

trigonal plane is composed of the $C\equiv C$ π-ligand and two chloride ligands, the pyramid being completed by a long Cu–Cl apical bond. In $[CuCl(HC\equiv CC_6H_5)]$ (**1**) (*cf.* Fig. 1 and Table 5), the copper(I) centre is displaced 0.14 Å from the plane through *X*, the midpoint of the C(1)–C(2) bond, Cl and Cl^{i} towards the apical chloride Cl^{ii} (for symmetry code, see Table 5). The $C\equiv C$ linkage is twisted 11° out of the plane through X, Cl and Cl^{i}. The Cl–Cu–X and Cl^{i}–Cu–X angles (Table 5) are, moreover, indicative of some $C\equiv C$ sliding [30] with respect to the trigonal plane. Similarly, in $[CuCl(HC\equiv CCH_2Cl)]$ (**2**) (*cf.* Fig. 2 and Table 6), Cu is displaced 0.14 Å from the plane through X, Cl(1) and Cl(1^{iii}) towards Cl(1^{iv}) while the $C\equiv C$ linkage is twisted 7° out of the trigonal plane. Again, the discrepancy between the Cl(1)–Cu–X and Cl(1^{iii})–Cu–X angles indicates $C\equiv C$ sliding [30] (for symmetry code, see Table 6). In $[CuCl(HC\equiv CCH_2OH)]$ (**3**), Fig. 3 and Table 7, Cu is again displaced 0.14 Å from the X, Cl, Cl^{v} plane towards the apical chloride (Cl^{vi}) and the acetylene linkage is twisted 3° out of this plane, some sliding [30] being indicated by the X–Cu–Cl and X–Cu–Cl^{v} angles.

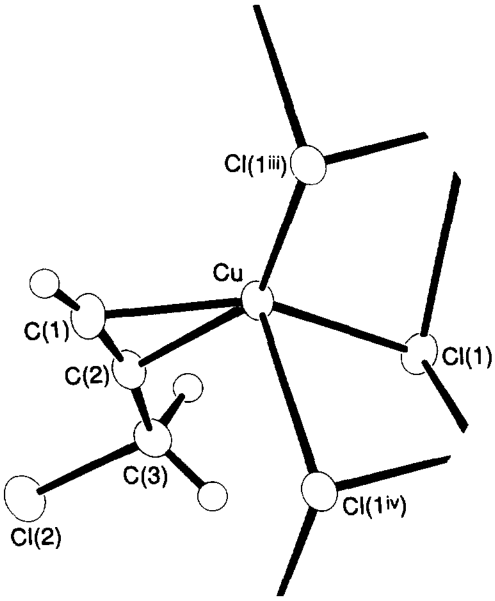

Fig. 2. Part of the chain in $[CuCl(HC\equiv CCH_2Cl)]$, **2**, showing the crystallographic numbering. For symmetry code, see Table 6. Thermal ellipsoids enclose 50% probability.

The Cu–C bond lengths, 1.999(4) and 2.066(3) Å in **1**, 2.004(3) and 2.004(4) Å in **2** and 2.006(10) and 2.018(9) Å in **3**, are in the range observed previously for π-alkyne complexes of copper(I) [2–17]. The phenylacetylene ligand in $[Cu(phen)(HC\equiv CC_6H_5)][ClO_4]$ [16] is also asymmetrically bonded to copper(I) as in **1**, with Cu–C distances of 1.922(12) and 1.995(10) Å to the α and β-carbon atoms of the ligand, respectively. The dihedral angle between the least-squares plane through the phenyl ring and that through X, Cl and Cl^{i} in **1** is 138°, closely similar to the corresponding value (142°) for $[Cu(phen)(HC\equiv CC_6H_5)][ClO_4]$ [16].

In **1**, four- and eight-membered Cu–Cl rings are fused to form layers (cf. Fig. 4), the Cu–Cl framework being reminiscent of that in the complex between copper(I) chloride and 1,7-octadiyne [15]. In **2**, Fig. 5, four-membered Cu–Cl rings are fused to form chains such as those in $[Cu_2Cl_2(C_6H_{10})]$, the complex between copper(I) chloride and dimethylbutadiene [19, 22]. The third complex, **3**, (cf. Fig. 6) has a Cu–Cl framework composed of six-membered rings such as those in the complex between isoprene and copper(I) chloride [18], the resulting layers being linked to form a three-dimensional network *via* hydrogen bonds involving the alcohol function ($O \cdots O^{vii,viii} = 2.741(9)$ Å; for symmetry code see Table 7).

There has been shown to be an almost linear rela-

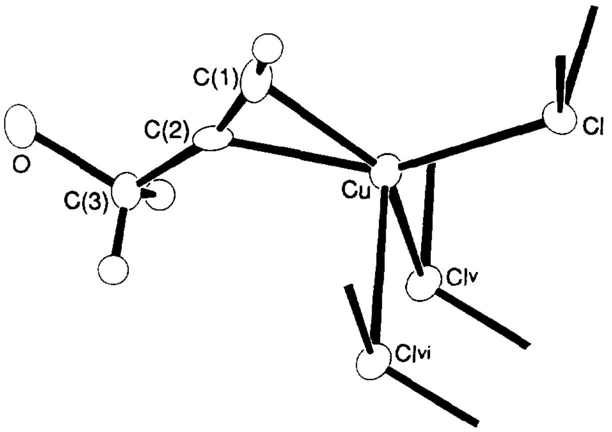

Fig. 3. Part of the layer of $[CuCl(HC\equiv CCH_2OH)]$, **3**, showing the crystallographic numbering. For symmetry code, see Table 7. Thermal ellipsoids enclose 50% probability.

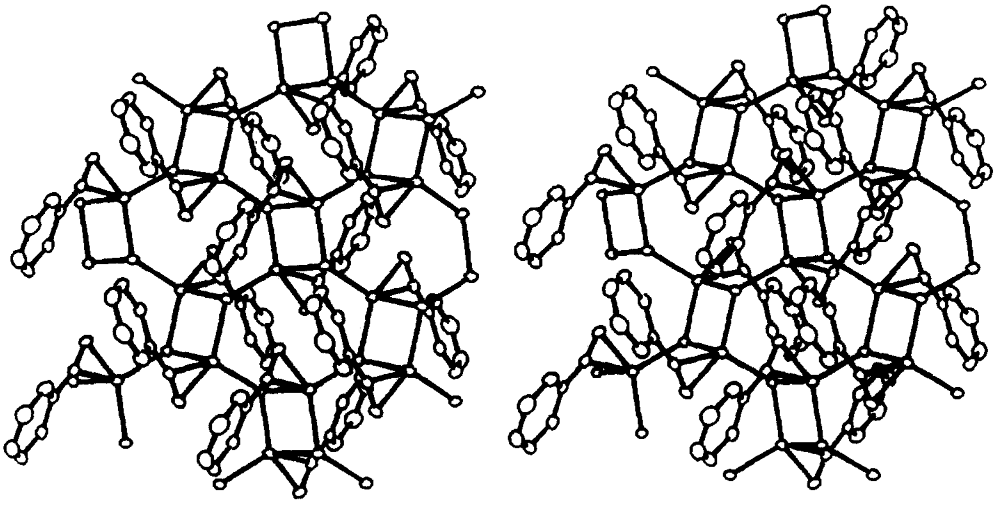

Fig. 4. Stereoview of [$CuCl(HC{\equiv}CC_6H_5)$], 1.

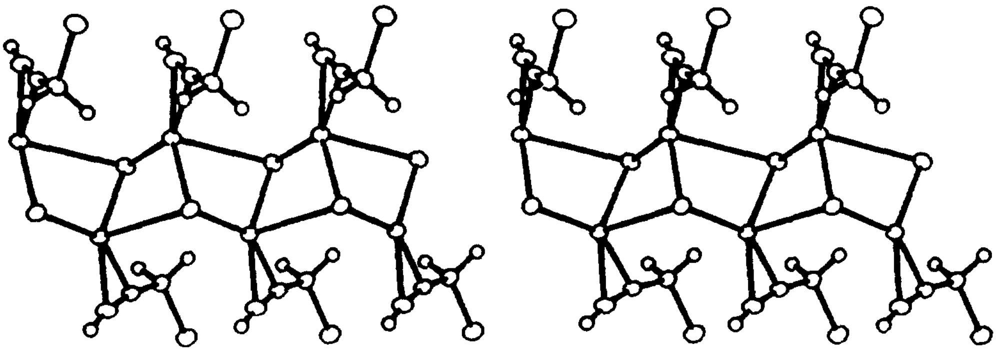

Fig. 5. Stereoview of [$CuCl(HC{\equiv}CCH_2Cl)$], 2.

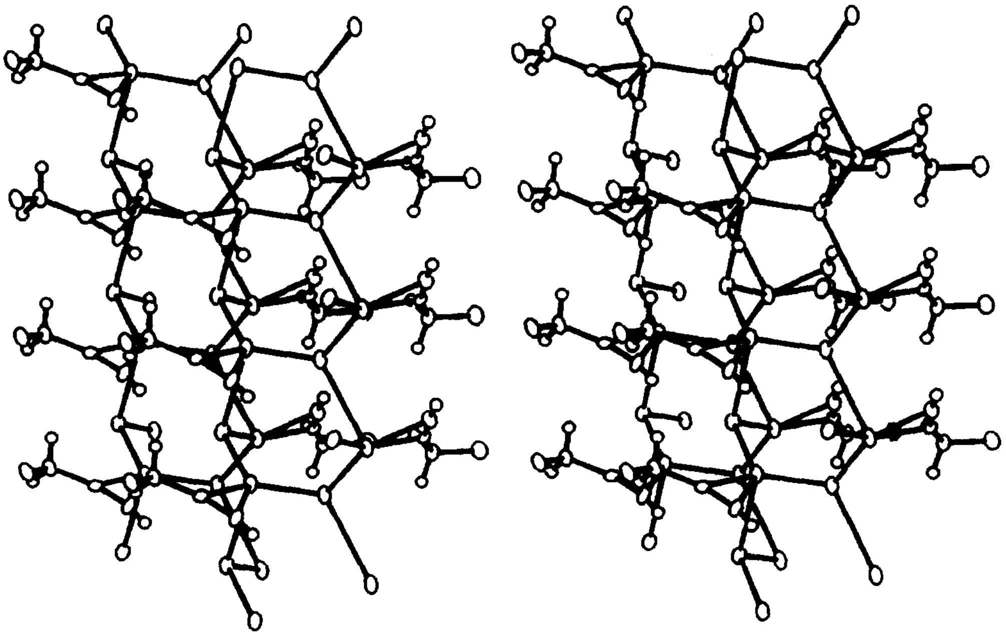

Fig. 6. Stereoview of [$CuCl(HC{\equiv}CCH_2OH)$], 3.

tionship between $\Delta\nu(C\equiv C)$ and the bending-back angle in π-acetylenic complexes of the transition metals [16,31], copper(I) complexes generally exhibiting small $\Delta\nu(C\equiv C)$ shifts and low values for bending-back angles (*cf.* ref. 16). The somewhat lower values of $\Delta\nu(C\equiv C)$ for the present complexes relative to those for other π-acetylenic complexes of copper(I) (*cf.* Table 8), suggest that the alkyne is even more weakly bound in the present complexes. The deviation of the H–C≡C and R–C≡C angles from linearity is usually considered to reflect the degree of back-bonding, *i.e.* metal ⇒ π^*-ligand transfer. In the complexes between copper(I) and 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne [12,13, 17], the R–C≡C angles are similar to that (145.8°) for the free acetylene [32], the lowering of $\nu(C\equiv C)$ indicating, however, appreciable copper(I)–ligand interaction [12,13,17]. The DEAD ligand in $[Cu_4(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}Cl)_4(\mu\text{-DEAD})_2]$ [10] and $[Cu_2(TC\text{-}6,6)(\mu\text{-DEAD})]$ [6,8] acts as a four-electron donor, bridging two copper(I) centres, resulting in longer C≡C distances and larger bending-back angles than for the remaining complexes. A similar result was found for $[Cu_2(TC\text{-}6,6)(\mu\text{-DMAD})]$ [8]. Theoretical evidence has been provided for appreciable participation of the second acetylene π orbital for transition metal alkyne complexes in which the ligand can be regarded as being a four-electron donor [33].

In general, the interaction between copper(I) and C≡C has been interpreted as consisting mainly of the σ component, *viz.* donation from the occupied π orbitals of the alkyne to the copper(I) centre. A theoretical study of the interaction of acetylene with Cu^+ indicates that π-back-bonding is negligible in the $(CuC_2H_2)^+$ ion [34]. From the relative constancy of the bending-back angles, and, in particular, deviation of the H–C≡C angle from linearity in the majority of the copper(I) complexes tabulated in Table 8, it would seem that the somewhat stronger alkyne–copper(I) interaction indicated by the larger $\Delta\nu(C\equiv C)$ values in *e.g.* the series of phenanthroline complexes than in the

TABLE 8. Structural data for some π-alkyne complexes of copper(I)

Complex	$d(C\equiv C)$ [a]	$\Delta\nu(C\equiv C)$ [b]	H–C≡C [c]	R–C≡C [c]	Ref.
$[CuCl(HC\equiv CPh)]$	1.213(5)	133	12(3)	17.1(3)	This work
$[CuCl(HC\equiv CCH_2Cl)]$	1.204(5)	144	14(4)	13.1(3)	This work
$[CuCl(HC\equiv CCH_2OH)]$	1.20(1)	154	12(9)	18(1)	This work
$[Cu_2Cl_2(HC\equiv C(CH_2)_4C\equiv CH)]$	1.196(9)	135	2(4)	11.6(6)	15
$[Cu\{NH(C_5H_4N)_2\}(HC\equiv CH)]^+$	1.188(11)	179	16(3)	–	4, 5
$[Cu(phen)(HC\equiv CH)]^+$ [d]	1.190(7)	174	15(3)	–	16
$[Cu(phen)(HC\equiv CPh)]^+$ [d]	1.218(13)	195	15(3)	17.2(12)	16
$[Cu(phen)(HC\equiv CCO_2Et)]^+$ [d]	1.193(10)	223	15(3)	25.3(8)	16
$[Cu_2Cl_2(Me_3SiC\equiv CSiMe_3)]$	1.227(5)	160	–	15.8(3) 13.7(3)	2
$[\{Cu(PhCO_2)(PhC\equiv CPh)\}_2]$	1.224(18)	195	–	21.5(7)	3
$[Cu(hfac)(PhC\equiv CPh)]$ [e]	1.246(13)		–	21.6(8) 19.6(8)	14
$[Cu_4(O_2CCF_3)_4(\mu\text{-}EtC\equiv CEt)_2]$	1.26(2)		–	24(2)–32(2)	11
$[Cu_2(TC\text{-}6,6)(\mu\text{-DEAD})]$ [f,g]	1.320(6)		–	41.3(4) 43.1(4)	6, 8
$[Cu_2(TC\text{-}6,6)(\mu\text{-DMAD})]$ [f,h]	1.314(9)		–	41.8(4) 41.0(7)	8
$[Cu_4(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}Cl)_4(\mu\text{-DEAD})_2]$ [f]	1.288(6)		–	31.6(7)	10
$[Cu(TBC)(OTf)_2]$ [i]	1.222(10)	123	–	2.2(6)	7
$[Cu_3(TBC)(OTf)_3]\cdot C_6H_6$ [i]		150	–	17.0(8) 14.0(8)	9
$[Cu_2(SPh)_2(tmtch)_2]$ [j]	1.230(5) 1.223(4)	230, 220	– –	– [k]	12
$[Cu_2Cl_2(tmtch)_2]$ [j]	1.220(6)	193, 189	–	– [l]	13
$[Cu_2Cl_2(tmtch)(CH_3SCH_3)]$ [j]	1.212(9)	194, 190	–	– [m]	13
$[Cu_2(OPh)_2(tmtch)_2]$ [j]	1.247(5)	245, 215	–	– [n]	17, 13
$[Cu_4(OOCMe)_4(tmtch)_2]$ [j]	1.259(7)	204, 203	–	– [o]	17, 13

[a] Å; [b] cm^{-1}; [c] bending-back angle (°), *i.e.* deviation from 180°; [d] phen = 1,10-phenanthroline; [e] hfac = hexafluoroacetylacetonate; [f] DEAD = diethyl acetylenedicarboxylate; [g] TC-6,6 = tropocoronand-6,6; [h] DMAD = dimethyl acetylenedicarboxylate; [i] TBC = 1,2 : 5,6 : 9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne; $OTf^- = O_3SCF_3^-$; [j] tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne; [k] R–C≡C angles 145.9(4)–147.8(4)° similar to the value for the free ligand *viz.* 145.8° [32]; [l] R–C≡C angles 147.3(5), 147.9(5)° (*cf.* free ligand [[32]); [m] R–C≡C angles 147.8(6), 147.8(6)° (*cf.* free ligand [32]); [n] mean R–C≡C angle 146.9(3)° (*cf.* free ligand [31]); [o] mean R–C≡C angle 142.7(5)° (*cf.* free ligand [32]).

present chloride complexes is mainly due to enhanced forward bonding. However, in $[Cu(OR)(tmtch)]_2$,R = Me, Ph [17], the back-bonding component is enhanced relative to that in the corresponding chloro complex [13] as a result of the presence of the basic Cu(OR) fragment [17]. Similarly, the slight increase in $\Delta\nu(C{\equiv}C)$ as R is changed from C_6H_5 through CH_2Cl to CH_2OH in the present series **1** to **3** might, as expected, indicate a concomitant increase in the back-bonding component; the constancy of the bending-back angles would, however, be more consistent with an increase in the forward (ligand ⇒ metal) bonding component, which is hardly realistic. Thus, one is forced to question the adequacy of the bending-back angle as an indicator of a specific bonding component. In any event, the metal–ligand interaction in the present complexes must be considered to be very weak.

As in the complexes between 1,7-octadiyne and copper(I) trifluoromethanesulfonate [1] and copper(I) chloride [15], respectively, $\nu(C_{sp}{-}H)$ is lowered relative to that for the free ligand in **1**–**3**. The shift in **2** (83 cm^{-1}) is comparable to that found for the former complex (81 cm^{-1}) whereas those for **1** and **3**, 120 cm^{-1} and 110 cm^{-1} are somewhat larger and are similar to the value of 117 cm^{-1} found for the complex between copper(I) chloride and 1,7-octadiyne [15]. For solutions, such shifts have been interpreted as indicating activation of the acetylenic C–H bond [1]. As is seen in Table 8, in the solid state, these shifts are accompanied by moderate $H{-}C{\equiv}C$ bending-back angles and by no means abnormal C–H distances or $Cu \cdots H$ contacts (cf. Tables 5–7). Obviously, errors associated with the location of hydrogen atoms by X-ray diffraction are large, but the trends exhibited by the structural data now available cannot be considered to provide evidence for appreciable $C{\equiv}C{-}H$ and $C_{sp}{-}H$ activation by copper(I) in the solid state.

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