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Synthesis and crystal structure of a polymeric complex between 1-penten-3-one and copper(I) chloride

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Abstract

Chloro[1–2-η-(1-penten-3-one)]copper(I) has been prepared by reaction between 1-penten-3-one and copper(I) chloride, and its structure determined by single-crystal X-ray diffraction at 170 K. [CuCl(C_5H_8O)], $M_r = 183.1$, crystallizes in space group $P2_1/c$ with a 7.129(3), b 9.089(3), c 10.480(3) Å, β 92.2(2)° and $Z = 4$. Full-matrix least-squares refinement of 105 structural parameters gave $R = 0.036$ for 1062 observed ($I > 3\sigma(I)$) reflections. In the complex between 1-penten-3-one and copper(I) chloride, copper(I) is four-coordinated, by two chloride ligands, the C=C bond of one pentenone ligand and, via a long Cu–O bond of 2.606(6) Å, by the carbonyl oxygen of another pentenone ligand. The structure can thus be described in terms of chloride-bridged dimers, which are joined, by pentenone bridges involving long Cu–O bonds, to form layers. The copper(I) coordination polyhedron is a trigonal pyramid in which the copper atom is displaced 0.134(2) Å towards the apical oxygen atom from the plane through the two chloride ligands and the midpoint of the C=C double bond. Cu–C distances are 2.048(6) and 2.060(6) Å; C=C is 1.383(8) Å. The pentenone ligand is planar and has the *s-cis* conformation.

Introduction

π-Complexation between copper(I) and α,β-unsaturated carbonyl compounds is of interest in connection with the promotion of conjugate addition reactions by copper(I) [1,2]. Recently, evidence for the formation of a π-intermediate in the reaction between cinnamic acid esters and lithium dimethylcuprate(I) was obtained from ^1H and ^{13}C NMR spectra [3] and a model for the transition state suggested [4]. Little is known, however, about the structures of π-complexes between α,β-unsaturated carbonyls and copper(I) compounds, in general, e.g. with respect to coordination geometry of copper(I), to preferential coordination of the α,β-un-

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saturated carbonyl ligand to copper(I) via the C=C double bond and the carbonyl oxygen atom contra coordination solely through C=C, and to the preferred conformation of the α,β-unsaturated carbonyl ligand. As part of an investigation on the formation and structure of such complexes, we have prepared a polymeric complex between copper(I) chloride and acrylaldehyde [5] and a tetrameric complex between copper(I) chloride and 3-buten-2-one [6]. In the former compound, the acrylaldehyde ligand has the *s-trans* conformation, and acts as a bridge, via the C=C double bond and the carbonyl oxygen atom, between adjacent copper(I) atoms [5]. In the latter compound there are two types of butenone ligand: one bridging, with the *s-trans* conformation, and one terminal, with the *s-cis* conformation, bonded to copper(I) solely via the C=C double bond [6]. We now report the preparation and structural characterisation of a π-complex between copper(I) chloride and 1-penten-3-one.

Experimental

Preparation of chloro[1–2-η-(1-penten-3-one)]copper(I). All operations were carried out under nitrogen or argon, by standard vacuum-line techniques. 1-Penten-3-one (Fluka pract.) was dried with 3 Å molecular sieves, then distilled and deoxygenated. Copper(I) chloride was purified by a standard method [7], then dried under reduced pressure under argon.

Approximately 10 ml 1-penten-3-one was distilled into a Schlenk tube containing 15 mmol copper(I) chloride. The tube was cooled to −25 °C and the mixture stirred vigorously, to give a yellow solution. Undissolved copper(I) chloride was filtered off and the filtrate transferred to one of the ends of an inverted U-shaped Schlenk tube. The solution was kept at −25 °C and the other end of the Schlenk tube at −196 °C, and pale-yellow prisms of $[CuCl(C_5H_8O)]$, suitable for X-ray analysis, were obtained after a few weeks.

Crystal and intensity data. C_5H_8ClCuO, $M_r = 183.1$, monoclinic, space group $P2_1/c$ (No. 14), a 7.129(3), b 9.098(3), c 10.480(3) Å, β 92.2(2)°, $Z = 4$, D_c 1.79 g cm^{-3}, μ(Mo-K_α) 3.62 mm^{-1}.

Owing to rapid loss of the pentenone ligand from the compound, even at −25 °C, as well as the sensitivity of the compound towards oxygen and water-vapour, the crystals were transferred to a Dewar vessel adapted for mounting crystals in glass capillaries at low temperature and in an inert atmosphere. A crystal was selected and cut at −60 °C, under a small amount of mother-liquor, then cooled rapidly to −110 °C and mounted in a glass capillary, 0.5 mm in diameter, containing pentenone and filled with argon. The capillary was sealed and transferred to the diffractometer, care being taken to keep the temperature of the capillary below −100 °C.

Intensity data from a crystal, cut to the approximate dimensions 0.2 × 0.2 × 0.2 mm, were measured at −105 °C for $2\theta < 50°$ with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo-K_α radiation. The ω–2θ scan mode was used with a variable 2θ scan rate of 3.0–15.0° min^{-1}. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method [8] was used to calculate the intensities [9]. Of the 1207 independent reflections measured, 1062 had $I > 3\sigma(I)$ and were considered observed. Unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

Table 1

Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms in chloro[1-2-η-(1-penten-3-one)]copper(I) [a]

Atom	x	y	z	B_{eq}
Cu	−0.01660(6)	0.35106(5)	0.06067(4)	1.95(1)
Cl	0.23806(13)	0.47276(10)	−0.00856(9)	2.30(2)
C(1)	0.0663(6)	0.1677(5)	0.1612(4)	2.6(1)
C(2)	−0.1262(6)	0.1833(4)	0.1669(4)	2.1(1)
C(3)	−0.2143(6)	0.2606(4)	0.2760(4)	2.1(1)
O	−0.1188(4)	0.3120(3)	0.3657(3)	2.5(1)
C(4)	−0.4251(6)	0.2699(5)	0.2693(4)	2.6(1)
C(5)	−0.5091(7)	0.3546(5)	0.3776(5)	2.8(1)

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

Structure determination and refinement. The structure was solved by direct methods (MITHRIL [10]; DIRDIF [11]). Full-matrix least-squares refinement of positional and isotropic thermal parameters gave an R value of 0.095; after empirical correction for the effects of absorption [12], R was reduced to 0.060. Inclusion of anisotropic thermal parameters ($R = 0.047$), and, finally, of positional and isotropic thermal parameters for the hydrogen atoms, located from a difference map, gave an R value of 0.036 for 105 parameters and 1062 reflections. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [13] and the F_0 values were weighted according to $w = [\sigma^2(F_0) + 0.0004F_0^2]^{-1}$. The final difference map showed a maximum residual electron density of 0.54 e $Å^{-3}$. The computer programs were as described in refs. 14 and 15. Fractional coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1. Lists of observed and calculated structure factors, fractional coordinates and thermal parameters for the hydrogen atoms, connectivity relationships involving the hydrogen atoms, and anisotropic thermal parameters for the non-hydrogen atoms may be obtained from the authors.

Discussion

The complex formed between copper(I) chloride and 1-penten-3-one dissociates rapidly, with immediate loss of pentenone, when warmed from ca. −100 °C to ambient temperature. The presumably very weak interaction between copper(I) and pentenone is reflected in the virtual undistortion of the molecule on coordination. The ligand, which has the *s-cis* conformation, retains its planarity (cf. Table 3), there being no significant deviations of any of the atoms of the pentenone skeleton from the least-squares plane through the molecule. As in the acrylaldehyde and butenone analogues [5,6] and many other π-olefinic complexes of copper(I) (see e.g. ref. [5], and ref. therein), the C=C bond is only very slightly lengthened on coordination.

The crystal structure of chloro[1–2-η-(1-penten-3-one)]copper(I) can be described in terms of chloride-bridged $[Cu_2Cl_2(C_5H_8O)_2]$ dimers (Fig. 1) joined by pentenone bridges involving long Cu–O bonds 2.606(6) Å, to form layers parallel to b–c (Fig. 2). Copper(I) is thus four-coordinated by two chloride ligands, the C=C double bond of one pentenone ligand, and the carbonyl oxygen of an adjacent pentenone

Table 2

Interatomic distances (Å) and angles (°) involving the non-hydrogen atoms in chloro[1–2-η-(1-penten-3-one)]copper(I) [a]

Cu–X	1.934(6)	C(1)–C(2)	1.383(8)
Cu–C(1)	2.048(6)	C(2)–C(3)	1.500(6)
Cu–C(2)	2.060(6)	C(3)–O	1.232(6)
Cu–Cl	2.269(6)	C(3)–C(4)	1.504(8)
Cu–Cl^{i}	2.301(5)	C(4)–C(5)	1.514(7)
Cu–O^{ii}	2.606(6)	Cu...Cu^{i}	3.007(8)
X–Cu–Cl	129.7(2)	C(1)–C(2)–C(3)	121.7(4)
X–Cu–Cl^{i}	131.3(2)	C(2)–C(3)–O	121.6(4)
X–Cu–O^{ii}	87.2(2)	C(2)–C(3)–C(4)	115.9(4)
Cl–Cu–Cl^{i}	97.7(2)	C(4)–C(3)–O	122.5(4)
Cl–Cu–O^{ii}	103.3(2)	C(3)–C(4)–C(5)	114.6(4)
Cl^{i}–Cu–O^{ii}	92.4(2)	C(3)–O–Cu^{iii}	120.8(3)
Cu–Cl–Cu^{i}	82.3(2)		

[a] X is the midpoint of the C(1)–C(2) bond. Estimated standard deviations are given in parentheses. Symmetry code: (i): $\bar{x}, 1-y, \bar{z}$; (ii): $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii): $x, \frac{1}{2}-y, \frac{1}{2}+z$. The C–H bond distances lie in the range 0.80(6)–1.04(6) Å.

ligand. As in the acrylaldehyde and the butenone complexes [5,6], the copper(I) coordination polyhedron is distorted from a tetrahedron towards a trigonal pyramid, the distortion being largest in the present compound. Here the copper atom is displaced 0.134(2) Å from the plane through the chloride ligands and X, the midpoint of the C=C bond, towards the apical oxygen ligand. The corresponding displacement in the complex between acrylaldehyde and copper(I) chloride is 0.270(4) Å [5], while the displacements involving the two structurally non-equivalent copper atoms in the complex between butenone and copper(I) chloride are 0.326(9) and 0.306(2) Å, respectively [6].

The olefin bond appears to be symmetrically coordinated to copper(I): the Cu–C distances, 2.048(6) and 2.060(6) Å, do not differ significantly. There is also no evidence for sliding of the olefin group [17] in the trigonal plane: the difference between the X–Cu–Cl and X–Cu–Cl^{i} angles is barely significant (5σ). Owing to the low precision associated with the positions of the olefinic hydrogen atoms, it does not seem meaningful to speculate on the bending back [17] of these substituents on the basis of the torsion angles about C=C (cf. Table 3). The Cu–C(1)–C(2)–C(3) torsion angle of −94.4(4)°, however, appears to indicate [17] a slight bending back of the carbonyl carbon atom. The Cu–C distances are in good agreement with those in the acrylaldehyde and butenone analogues [5,6]. The bridging Cu–O bond, 2.606(6) Å, is, however, longer than in either of the latter complexes (2.296(6) Å in

Table 3

Selected torsion angles (°) in chloro[1–2-η-(1-penten-3-one)]copper(I) [a]

Cu–C(1)–C(2)–C(3)	−94.4(4)	C(1)–C(2)–C(3)–O	−0.8(5)
Cu–C(1)–C(2)–H(2)	95(4)	C(1)–C(2)–C(3)–C(4)	179.8(6)
Cu–C(2)–C(1)–H(11)	104(4)	C(2)–C(3)–C(4)–C(5)	−177.3(5)
Cu–C(2)–C(1)–H(12)	−90(5)	C(2)–C(3)–O–Cu^{iii}	−86.0(4)

[a] Estimated standard deviations are given in parentheses. Symmetry code: (iii): $x, \frac{1}{2}-y, \frac{1}{2}+z$.

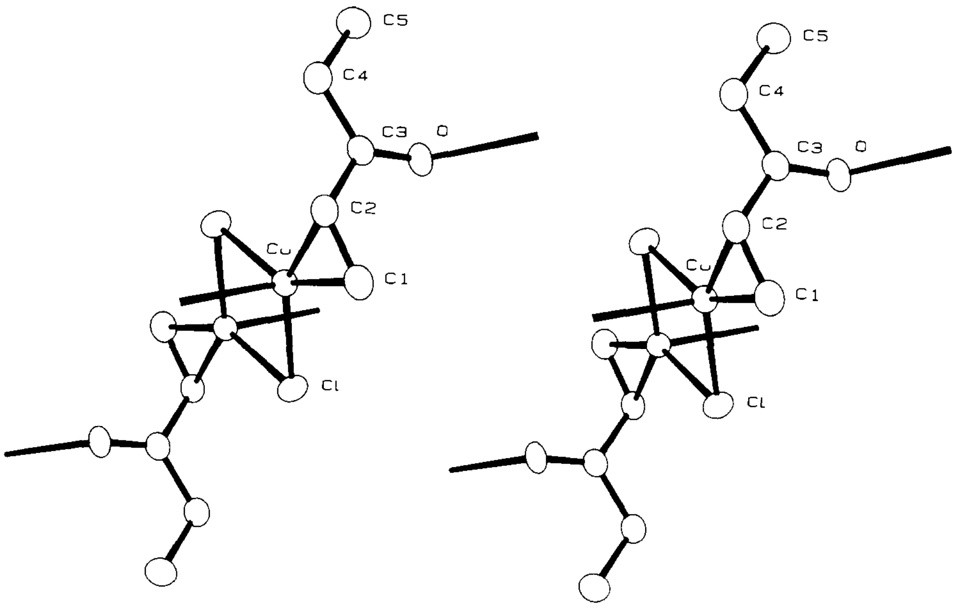

Fig. 1. Stereoscopic view [16] of the $[Cu_2Cl_2(C_5H_8O)_2]$ unit in chloro[1-2-η-(1-penten-3-one)]copper(I). The thermal ellipsoids enclose 50% probability.

$[CuCl(C_3H_4O)]$ [5] and 2.33(2) Å in $[Cu_4Cl_4(C_4H_6O)_4]$ [6]) and considerably longer than the Cu–O bonds in the π-complex between copper(I) chloride and allyl alcohol, 2.076(7) Å, [18] and in copper(I) hydrogen maleate monohydrate, 1.999(6) Å, in which copper(I) is also bonded to C=C [19]. Long copper(I)–oxygen bonds in distorted tetrahedral coordination environments are found in the copper(I) trifluo-

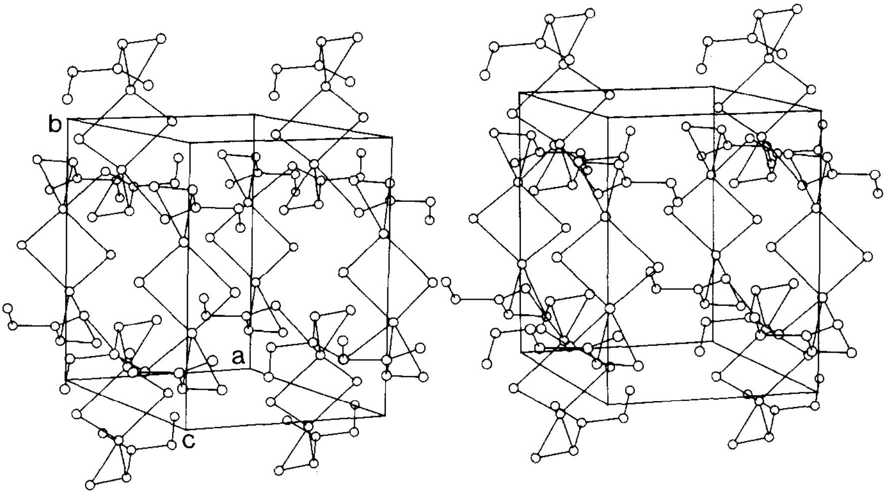

Fig. 2. Stereoscopic view [16] of the structure of $[CuCl(C_5H_8O)]$ showing connection of the dimeric units to form layers via long Cu–O bonds. All atoms are represented as spheres of radius 0.10 Å.

romethanesulphonate cyclohexene complex, 2.587(6) Å [20], and in the mixed-valence complex $[Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)]$, 2.524(7) Å [21].

The C=O bond length, 1.232(6) Å, is normal; the C(3)–O–Cu^{iii} angle, 120.8(3)° (for symmetry code see Table 2) is similar to that found in $[Cu_4Cl_4(C_4H_6O)_4]$, viz. 124(1)° [6], both values being considerably smaller than that at the bridging oxygen atom in $[CuCl(C_3H_4O)]$, 140.0(6)° [5]. Cu^{iii} lies 2.239(5) Å from the least-squares plane through the bridging pentenone ligand, and the C(2)–C(3)–O–Cu^{iii} torsion angle, −86.0(4)°, is very much larger than the corresponding angle involving the *s-trans* acrylaldehyde bridge, 27(1)° [5], or the *s-trans* butenone bridge, 37(2)° [6].

The ratio between the *s-cis* and *s-trans* conformers of uncomplexed 1-penten-3-one is 0.61, i.e. 38% *s-cis*, at 35 °C [22]. Similarly, the *s-trans* conformer of 3-buten-2-one is the more stable conformer at ambient temperature, the ratio of *s-cis* to *s-trans* decreasing with decreasing temperature, e.g. 0.68 at 14 °C and 0.23 at −56 °C [23]. In acrylaldehyde the *s-trans* conformer appears to predominate markedly over the *s-cis* [22,24–26], and the molecule exists exclusively as the *s-trans* conformer in carbon tetrachloride at 35 °C. On complexation with copper(I) chloride, 1-penten-3-one assumes the *s-cis* conformation exclusively (Fig. 1, Table 3), whereas in the butenone analogue [6], the bridging butenone ligand is *s-trans* while that bonded to copper solely via C=C is *s-cis*. Acrylaldehyde retains the preferred *s-trans* conformation of the free molecule when bridging adjacent copper(I) atoms in the complex with copper(I) chloride [5]. Accepting the Cu–O distance of 2.606(6) Å in the present compound as representing a weak interaction, it is conceivable that *s-cis* is the preferred conformation of this class of ligand when the primary bonding interaction to copper(I) is through the C=C double bond.

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