Preparation and Structural Characterisation of a Tetrameric Complex Between 3-Butene-2-one and Copper(I) Chloride

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Bis[μ-(3-butene-2-one-3-4-η,O)]bis[3-4-η-(3-butene-2-one)]tetra-μ-chloro-tetra-copper(I) was prepared from copper(I) chloride and 3-butene-2-one, and the structure of the compound was determined from X-ray diffractometer data. [Cu$_4$Cl$_4$(C$_4$H$_6$O)$_4$], M_r = 676.4, crystallizes in space group $P\bar{1}$, with a = 9.138(6), b = 10.603(10), c = 6.324(4) Å, α = 99.62(6)°, β = 98.90(5)°, γ = 81.09(6)° and Z = 1, the crystals being extremely unstable with respect to loss of butenone. Full-matrix least-squares refinement of 127 structural parameters gave R = 0.10 for 1093 independent observed [I > 3.0σ(I)] reflections. The [Cu$_4$Cl$_4$(C$_4$H$_6$O)$_4$] tetramer is centrosymmetric and contains two crystallographically independent copper(I) atoms, bridged by a butenone ligand and two chloride ligands, the remaining ligand being terminally bonded to one of the copper(I) atoms through the olefin group. One of the copper(I) atoms can thus be regarded as being three-coordinated by two chloride ligands and the C=C double bond of the bridging butenone ligand. The other is approximately tetrahedrally coordinated by two chloride ligands, the C=C double bond of the terminal butenone ligand and the carbonyl oxygen of the bridging butenone ligand. Whereas the bridging butenone ligand has the s-trans conformation, the conformation of the terminal ligand is s-cis. Catenation of the tetramers along c is afforded by Cu···Cl interactions of 2.724(4) Å.

π-Complexes between copper(I) and α,β-unsaturated carbonyl compounds are of interest in connection with the tendency of copper(I) to promote conjugate addition reactions.[1,2] Recently, we prepared a polymeric compound between acrylaldehyde and copper(I) chloride and determined its crystal structure.[3] We now report the preparation and structural characterisation of a complex between butenone and copper(I) chloride.

Experimental

A distillation apparatus was assembled by connecting a 100 ml flask, containing 3 Å molecular sieves, a condenser and a Schlenk tube, containing 15 mmol purified[4] copper(I) chloride. The apparatus was connected to a vacuum/nitrogen line through the stopcock of the Schlenk tube and ca. 20 ml butenone (Fluka pract.) was introduced under nitrogen into the flask. After connection of the condenser to a refrigerating system providing circulation of ethanol at −20 °C, approximately 10 ml butenone were distilled under reduced pressure into the Schlenk tube. The tube was removed and cooled to −50 °C, the mixture of cop-

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per(I) chloride and butenone being stirred vigorously, whereupon copper(I) chloride dissolved giving a deep yellow solution. This solution was allowed to stand at approximately 4 °C, a pale yellow microcrystalline solid being obtained after a few hours and pale yellow needles of [Cu₄Cl₄ (C₄H₆O)₄] after a few days.

Bis[μ-(3-butene-2-one-3-4-η,O)] bis [3-4-η-(3-butene-2-one)] tetra-μ-chloro-tetracopper(I), [Cu₄Cl₄(C₄H₆O)₄], M_r = 676.4, is triclinic, space group $P\bar{1}$, with a = 9.138(6), b = 10.603(10), c = 6.324(4) Å, α = 99.62(6)°, β = 98.90(5)°, γ = 81.09(6)°, Z = 1, D_c = 1.90 g cm⁻³ and μ(MoKα) = 4.15 mm⁻¹. Crystals of [Cu₄Cl₄(C₄H₆O)₄] decompose losing butenone within seconds of exposure to air. Despite numerous attempts, using crystals mounted in epoxy resin and crystals mounted in glass capillaries containing mother liquor, it has not yet been possible to obtain a completely satisfactory set of diffracted intensities, owing to the extremely rapid loss of the butenone ligand. The structure of the compound has been determined from diffracted intensities from a crystal, 0.18×0.19×0.31 mm, mounted in epoxy resin. A Syntex $P2_1$ diffractometer and graphite-monochromated MoKα radiation were employed, intensities being measured for 2θ < 45° using the ω scan mode with a variable 2θ scan rate of 3.5–29.3° min⁻¹. A 19-step profile was recorded for each reflection and the Lehmann and

Larsen profile-analysis method[5] was used to calculate the intensities.[6] The intensities of two reflections, 11$\bar{2}$ and 01$\bar{1}$, measured at regular intervals, dropped to 70 % and 65 % of their original values, respectively, during measurement (7.6 hours), the decay being approximately linear with time. Of the 1539 independent reflections measured, 1093 had I > 3.0 σ(I) and were considered observed. Intensities were corrected for Lorentz and polarisation effects and scaled on the basis of the measured intensities of the two standard reflections, assuming linear decay with time. An empirical correction[7] for the effects of absorption was made after solution of the structure. Unit-cell parameters were obtained from diffractometer setting angles for 15 reflections.

Structure determination and refinement

The positions of the copper and chlorine atoms and those of some of the light atoms were obtained by direct methods (MITHRIL)[8]; the remaining non-hydrogen atoms were located from a subsequent electron density map.[9] Full matrix least-squares refinement[9] of positional, isotropic and, subsequently, anisotropic thermal parameters gave R = 0.10 for 127 parameters and 1093 reflections. A difference map showed a maximum residual electron density of 1.1 eÅ⁻³. No attempt was made to locate the hydrogen

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å²) for the non-hydrogen atoms in bis[μ-(3-butene-2-one-3-4-η,O)] bis [3-4-η-(3-butene-2-one)] tetra-μ-chloro-tetracopper(I). B_{eq} is defined as $8π^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu(1)	0.0000(3)	0.5915(2)	0.2571(3)	3.68(8)
Cu(2)	0.2673(3)	0.2975(2)	0.3414(3)	3.53(7)
Cl(1)	0.0348(5)	0.3683(4)	0.1636(5)	3.1(1)
Cl(2)	0.2435(6)	0.3475(5)	0.7014(6)	3.7(1)
C(1)	0.351(2)	0.655(2)	0.099(3)	4.6(7)
C(2)	0.318(2)	0.575(2)	0.259(3)	3.4(6)
O(1)	0.382(2)	0.464(2)	0.268(2)	4.6(5)
C(3)	0.208(2)	0.629(2)	0.414(3)	3.6(6)
C(4)	0.120(2)	0.742(2)	0.410(2)	3.8(6)
C(5)	0.188(3)	0.026(2)	−0.136(4)	6.8(9)
C(6)	0.272(3)	0.048(2)	0.095(4)	5.7(8)
O(2)	0.254(3)	−0.013(2)	0.235(3)	9.2(9)
C(7)	0.371(2)	0.145(2)	0.140(3)	4.6(7)
C(8)	0.459(2)	0.166(2)	0.334(4)	5.0(7)
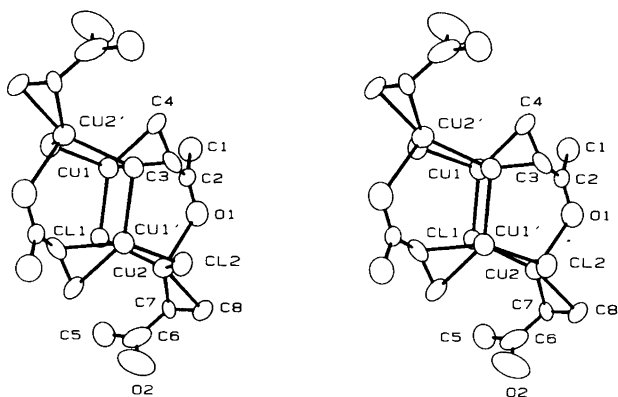
Fig. 1. Stereoscopic view[11] of the [$Cu_4Cl_4(C_4H_6O)_4$] tetramer showing the atomic numbering. Thermal ellipsoids enclose 50 % probability.[11] The primed atoms are at $\bar{x}$, 1-y, 1-z.

atoms. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*[10] and weights were calculated according to $w = [\sigma^2(F_o) + 0.0005\ F_o^2]^{-1}$. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1. Structure factors and anisotropic thermal parameters may be obtained from the authors.

A partial data set comprising 960 reflections [$0 \geq h \geq 4$, $-11 \geq k \geq 11$, $-6 \geq l \geq 6$] of which 875 were observed [$I > 3.0\ \sigma(I)$], obtained from a crystal which exhibited abrupt decay, yielded an identical structural model, within the limits of error, for which $R = 0.063$ (127 parameters; 875 reflections).

Discussion

The solubility of copper(I) chloride in butenone would appear to increase with decreasing temperature, a property which has been exploited in the preparation of the present complex. The crystal structure of the compound can be described in terms of [$Cu_4Cl_4(C_4H_6O)_4$] tetramers (Fig. 1) linked to form chains along c by Cu···Cl interactions of 2.727(4) Å (Fig. 2; Table 2). The four copper(I) atoms of the tetramer, Cu(1), Cu(2), Cu(1') and Cu(2'), (Fig. 1) are exactly co-planar, due to the crystallographic centre of symmetry, and are bridged by a butenone ligand, two chloride ligands and their symmetry-related counter-
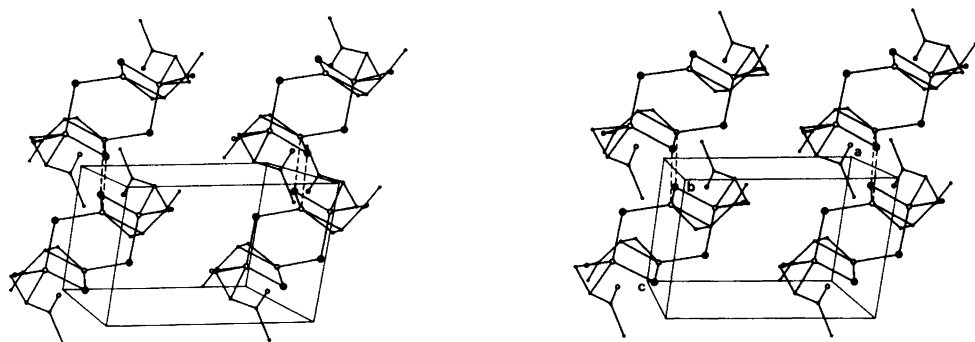

Fig. 2. Stereoscopic view[11] of the structure illustrating the linking of tetramers to form chains along c. The Cu···Cl distances of 2.727(4) Å are shown as broken lines. Copper atoms are depicted as open spheres of radius 0.07 Å and chlorine, carbon and oxygen as filled spheres of radius 0.09, 0.03 and 0.055 Å, respectively.

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Table 2. Interatomic distances (Å) and angles (°) in bis[μ-(3-butene-2-one-3-4-η,*O*)] bis [3-4-η-(3-butene-2-one)] tetra-μ-chloro-tetracopper(I). Estimated standard deviations are given in parentheses. X(1) and X(2) are the midpoints of the C(3)-C(4) and C(7)-C(8) bonds, respectively. Symmetry code: (*i*): *x̄*,1-*y*,1-*z*; (ii): *x̄*,1-*ȳ*,*z̄*.

Cu(1)-C(4)	2.10(2)	Cu(2)-C(8)	2.07(2)
Cu(1)-C(3)	2.07(2)	Cu(2)-C(7)	2.09(2)
Cu(1)-X(1)	1.97(2)	Cu(2)-X(2)	1.96(2)
Cu(1)-Cl(1)	2.326(5)	Cu(2)-Cl(1)	2.322(5)
Cu(1)-Cl(2ⁱ)	2.262(6)	Cu(2)-Cl(2)	2.286(4)
Cu(1)···Cl(1ⁱⁱ)	2.727(4)	Cu(2)-O(1)	2.33(2)
C(4)-C(3)	1.34(3)	C(8)-C(7)	1.37(3)
C(3)-C(2)	1.49(3)	C(7)-C(6)	1.43(3)
C(2)-C(1)	1.51(3)	C(6)-C(5)	1.54(3)
C(2)-O(1)	1.24(2)	C(6)-O(2)	1.23(3)
Cu(1)···Cu(2)	3.710(5)	Cu(1)···Cu(1ⁱ)	3.899(5)
Cu(1)···Cu(1ⁱⁱ)	3.497(5)	Cu(1)···Cu(2ⁱ)	3.719(4)
X(1)-Cu(1)-Cl(1)	121.5(6)	X(2)-Cu(2)-Cl(1)	127.8(7)
X(1)-Cu(1)-Cl(2ⁱ)	124.1(6)	X(2)-Cu(2)-Cl(2)	120.8(7)
X(1)-Cu(1)···(Cl(1ⁱⁱ)	106.9(5)	X(2)-Cu(2)-O(1)	96.8(7)
Cl(1)-Cu(1)-Cl(2ⁱ)	107.6(2)	Cl(1)-Cu(2)-Cl(2)	105.0(2)
Cl(1)-Cu(1)···Cl(1ⁱⁱ)	92.8(2)	Cl(1)-Cu(2)-O(1)	94.4(4)
Cl(2ⁱ)-Cu(1)···Cl(1ⁱⁱ)	94.9(2)	Cl(2)-Cu(2)-O(1)	104.5(3)
Cu(1)-Cl(1)-Cu(2)	105.9(2)	Cu(1ⁱ)-Cl(2)-Cu(2)	109.7(2)
Cu(1)-Cl(1)···Cu(1ⁱⁱ)	87.2(2)	Cu(1ⁱⁱ)···Cl(1)-Cu(2)	121.3(2)
C(4)-C(3)-C(2)	125(2)	C(8)-C(7)-C(6)	122(2)
C(3)-C(2)-C(1)	121(2)	C(7)-C(6)-C(5)	117(2)
C(3)-C(2)-O(1)	118(2)	C(7)-C(6)-O(2)	122(2)
C(1)-C(2)-O(1)	121(2)	C(5)-C(6)-O(2)	121(2)
Cu(2)-O(1)-C(2)	124(1)		

Table 3. Selected torsion angles (°) in bis[μ-(3-butene-2-one-3-4-η,*O*)] bis [3-4-η-(3-butene-2-one)] tetra-μ-chloro-tetracopper(I). Estimated standard deviations are given in parentheses. Symmetry code (*i*): *x̄*, 1-*y*, 1-*z*.

Cl(2ⁱ)-Cu(1)-Cl(1)-Cu(2)	−142.1(2)	Cl(1)-Cu(2)-Cl(2)-Cu(1ⁱ)	10.7(3)
Cu(1)-Cl(1)-Cu(2)-Cl(2)	64.6(2)	Cu(2)-Cl(2)-Cu(1ⁱ)-Cl(1ⁱ)	−104.6(3)
C(1)-C(2)-C(3)-C(4)	7(3)	C(5)-C(6)-C(7)-C(8)	−175(3)
O(1)-C(2)-C(3)-C(4)	−174(3)	O(2)-C(6)-C(7)-C(8)	6(3)
Cu(1)-C(4)-C(3)-C(2)	99(2)	Cu(2)-C(8)-C(7)-C(6)	− 96(2)
C(3)-C(2)-O(1)-Cu(2)	37(2)		

parts. The remaining butenone ligand is terminally bonded to Cu(2) through the olefin group.

Cu(1) can be regarded as being three-coordinated by Cl(1), Cl(2ⁱ) and the C=C double bond of the bridging butenone ligand (Table 2) or as having trigonal pyramidal coordination geometry if the Cu···Cl(1ⁱⁱ) interaction of 2.727(4) Å is taken into account. Cu(1) is displaced 0.326(9) Å

towards Cl(1ⁱⁱ) from the plane through Cl(1), Cl(2ⁱ) and X(1), the midpoint of the C(3)-C(4) bond. Similar coordination geometry has been observed for one of the copper(I) atoms in the [Cu₇Cl₁₀]³⁻ chain in tris(tetraethylammonium) *catena*-μ-chloro-ennea-μ-chloro-heptacuprate(I), the corresponding Cu···Cl distance and displacement of copper(I) from the trigonal plane being

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2.980(2) and 0.306(2) Å, respectively;[12] in [N(C$_2$H$_5$)$_4$]$_3$[Cu$_7$Cl$_{10}$], however, the Cu···Cl interaction is not a prerequisite for catenation.

Cu(2) is approximately tetrahedrally coordinated by two chloride ligands and the C=C double bond and the carbonyl oxygen of two different butenone ligands (Fig. 1, Table 2). As in the complex between acrylaldehyde and copper(I) chloride,[3] the ligand tetrahedron exhibits trigonal pyramidal distortion such that Cu(2) lies 0.31(1) Å from the plane through Cl(1), Cl(2) and X(2), the midpoint of the C(7)-C(8) bond; the corresponding value in [CuCl(C$_3$H$_4$O)] is 0.270(4) Å.[3]

Square-planar arrangements of copper(I) in tetrameric organocopper(I) compounds are not uncommon;[13,14] in the present tetramer the copper(I) atoms necessarily form a rhombus [Cu···Cu = 3.710(5) and 3.719(4) Å (Table 2) Cu(1)-Cu(2)-Cu(1^i) = 63.31(9)°] rather than a square, owing to inequality in size of the bridging ligands. Catenation of the tetramers *via* the Cu···Cl(1^{ii}) linkage affords a Cu···Cu separation of 3.497(5) Å.

The copper(I) and chlorine atoms of the tetramer can be considered to form an eight-membered ring which has a distorted chair conformation (Fig. 1, Table 3), reminiscent of the (Cu-X)$_4$ "step" cores in *e.g.* [P(C$_6$H$_5$)$_3$CuBr]$_4$·2CHCl$_3$[15] and [P(C$_6$H$_5$)$_3$CuI]$_4$.[16] In the present complex there are, however, no Cu-Cl bonds across the ring, the non-bonded intra-ring separation, Cu(1)···Cl(1^i) being 3.675(5) Å (symmetry code: (*i*): $\bar{x}$,1-*y*, 1-*z*).

Whereas the bridging butenone ligand retains the preferred *s-trans* conformation of the free molecule,[17] as does the acrylaldehyde ligand in [CuCl(C$_3$H$_4$O)],[3] the terminal butenone ligand in the present complex has the *s-cis* conformation (Fig. 1; Table 3). The magnitudes of the C(6)···Cu(2) and O(2)···Cu(2) distances: 2.83(2) and 3.27(2) Å, respectively, would appear to preclude η^4 coordination. Terminal η^2 coordination of the *s-cis* conformer of butenone has been documented for *e.g.* Mn(C$_5$H$_5$)(CO)$_2$(C$_4$H$_6$O),[18] and η^4 coordination for *e.g.* W(C$_4$H$_6$O)$_3$.[19]

That the thermal parameters associated with the terminal butenone ligand in [Cu$_4$Cl$_4$(C$_4$H$_6$O)$_4$] are somewhat higher than the values obtained for the bridging ligand, and that the former parameters were those most affected by scaling of in-

tensities, suggests that the terminal ligand is the more labile of the two. This is also in accordance with the considerably more rapid loss of ligand from [Cu$_4$Cl$_4$(C$_4$H$_6$O)$_4$] as compared with [CuCl (C$_3$H$_4$O)] in which acrylaldehyde acts solely as a bridge.[3]

At the present level of structural refinement, no differences can be detected between connectivity relationships within the two butenone ligands. Both ligands are essentially planar (Table 3). Copper(I)-carbon coordination distances do not differ either within or between the two ligands and are in good general agreement with values determined previously for π-olefinic complexes of copper(I) [see Ref. 3 and references therein]. The Cu(1)-C(4)-C(3)-C(2) and Cu(2)-C(8)-C(7)-C(6) torsion angles (Table 3) appear to indicate[20] a slight bending back of the carbonyl carbon atoms, as in [CuCl(C$_3$H$_4$O)].[3] Cu(2) lies 1.16(3) Å from the least-squares plane through the bridging butenone ligand and the C(3)-C(2)-O(1)-Cu(2) torsion angle is 37(2)°; the corresponding values in [CuCl(C$_3$H$_4$O)] are 0.86(3) Å and 27(1)°, respectively.[3] The Cu(2)-O(1)-C(2) angle, 124(1)°, is considerably smaller than that at the bridging oxygen atom in [CuCl(C$_3$H$_4$O)], *viz.* 140.0(6)°.[3]

In the complex between acrylaldehyde and copper(I) chloride, the olefin bond is symmetrically positioned with respect to the chloride ligands, *i.e.* the X-Cu-Cl angles do not differ (X = midpoint of C=C).[3] In the present complex, X(2)-Cu(2)-Cl(1) and X(2)-Cu(2)-Cl(2) appear to differ (Table 2). This might indicate sliding[20] of the olefin group of the terminal butenone ligand in such a way as to bring C(7) closer to the bisector of the Cl(1)-Cu(2)-Cl(2) angle. Olefin slipping has been shown to play a crucial rôle in activation of the C=C double bond.[21]

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