Structure of a Polymeric Complex Between Acrylaldehyde and Copper(I) Chloride

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An orthorhombic phase of chloro[2-3-η-(prop-2-en-1-al)] copper(I) was prepared from copper(I) chloride and acrylaldehyde and the structure of the compound determined from X-ray (MoKα) diffractometer data. [CuCl(C₅H₅O)] crystallizes in space group P2₁2₁2₁, with a = 8.722(4), b = 5.508(2), c = 9.828(4) Å and Z = 4. Full-matrix least squares refinement of 67 structural parameters gave R = 0.056 for 757 independent [I > 3.0σ(I)] reflections. Copper(I) is approximately tetrahedrally coordinated with Cu–C = 2.075(9) and 2.088(7), Cu–Cl = 2.289(2) and 2.294(2) and Cu–O = 2.296(6) Å, adjacent copper(I) atoms being bridged by acrylaldehyde and chloride ligands to form a three-dimensional network. The acrylaldehyde ligand is virtually undistorted and has C=C, C=O and C=O distances of 1.362(12), 1.485(10) and 1.230(9) Å, respectively.

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, and, in particular, selective conjugate addition. Evidence for the formation of a π-intermediate in the reaction between cinnamic acid esters and lithium dimethylcuprate(I) has been obtained recently from 1H and 13C NMR spectra. In order to provide more information concerning the coordination geometry of copper(I) in such complexes with a view to elucidating the role of copper(I) in the promotion of conjugate addition, we are attempting to prepare crystalline model compounds of these labile intermediates for investigation by single-crystal X-ray diffraction. Crystals of a complex between copper(I) chloride and acrylaldehyde have been obtained previously by direct reaction and the structure of the compound discussed in relation to its IR spectrum. A note on the X-ray structural analysis of this phase, which is monoclinic with a = 8.48(2), b = 17.18(2), c = 6.52(2) Å, β = 100.0(5)°, space group P2₁/c and Z = 8, indicates that acrylaldehyde acts as a bridge between two copper atoms, one of the two crystallographically independent copper atoms apparently being involved in Cl–Cu–Cl chains and the other in (Cu–Cl)₂ rings.

We prepared an orthorhombic phase of chloro[2-3-η-(prop-2-en-1-al)]copper(I) from copper(I) chloride and acrylaldehyde and undertook a crystal-structure determination.

Experimental

A distillation apparatus was assembled by connecting a 100 ml flask, containing 4 Å molecular sieves, a condenser and a Schlenk tube, containing 10 mmol purified copper(I) chloride; the apparatus was connected to a vacuum/nitrogen line through the stopcock of the Schlenk tube and ca. 20 ml acrylaldehyde (Fluka pract.) was introduced under nitrogen into the flask. After connection of the condenser to a refrigerating system

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providing circulation of ethanol at −20°C, approximately 10 ml acryaldehyde was distilled under reduced pressure into the Schlenk tube. The yellow solution and yellow microcrystalline solid thus obtained were separated under nitrogen at room temperature. The solution was allowed to stand under nitrogen at approximately 4°C, pale-yellow irregular-shaped plates being deposited after a few days. A further crop of crystals was deposited from a solution obtained by dissolving the microcrystalline solid in acryaldehyde under nitrogen. Crystals of [CuCl(C_3H_5O)] decompose losing acryaldehyde within seconds of exposure to air.

Crystals of chloro[2-3-η-(prop-2-en-1-αl)] copper(I), [CuCl(C_3H_5O)], M_r = 155.1, are orthorhombic, space group P2_12_1, a = 8.722(4), b = 5.508(2), c = 9.828(4) Å, Z = 4, D_r = 2.18 g cm\(^{-3}\), μ(MoKα) = 5.18 mm\(^{-1}\). A crystal, 0.57×0.28×0.27 mm, was mounted rapidly in epoxy-resin and diffracted intensities were measured immediately at approximately 18°C for 2θ < 60° with a Syntex P2_2_2, diffractometer using graphite-monochromated MoKα radiation and the ω-2θ scan mode with a variable 2θ scan rate of 3.5–29.3°min\(^{-1}\). A 96-step profile was recorded for each reflection and intensities were calculated according to refs. 7 and 8. Of the 800 independent reflections measured, excluding those systematically absent, 757 had I > 3.0 σ(I) and were regarded as being observed. That the crystal was not subject to decay under the approximately 7 h during which intensities were measured was checked by monitoring two reflections at regular intervals. Intensity data were corrected for Lorentz and polarization effects but not for absorption. Unit-cell parameters were obtained from diffractometer setting angles for 15 reflections.

**Structure determination and refinement**

The coordinates of the copper and chlorine atoms were obtained from the Patterson function and those of the carbon and oxygen atoms from a subsequent electron-density map. Full-matrix least-squares refinement of positional and isotropic thermal parameters yielded R = 0.080. Inclusion of anisotropic thermal parameters (R = 0.059) and, finally, of positional parameters for the hydrogen atoms, located from a difference map, the isotropic thermal parameters of the hydrogen atoms being set equal to the equivalent isotropic values of the carrying carbon atoms (Table 1) gave R = 0.056 (67 parameters; 757 reflections). R based on all 800 reflections, with the I < 3.0 σ(I) reflections at their measured values, was 0.057. Atomic scattering factors were taken from ref. 9 and the F_w values were weighted according to w = [σ(F_w) + 0.0095F_w]^\(-1\). A final difference map showed a maximum residual electron density of 0.90 eÅ\(^{-3}\). The computer programs used are described in ref. 10. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 1. Observed and calculated structure factors, fractional coordinates for the hydrogen atoms, carbon-hydrogen bond lengths and anisotropic thermal parameters for the non-hydrogen atoms may be obtained from the authors.

**Discussion**

In chloro[2-3-η-(prop-2-en-1-αl)]copper(I), adjacent copper(I) atoms are bridged by acryaldehyde, in the s-trans conformation, and chloride ligands to form a three-dimensional network (Figs. 1 and 2). Bond distances seem to be in general agreement with those noted previously:

### Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å\(^2\)) for the non-hydrogen atoms in [CuCl(C_3H_5O)]. B_\(\text{eq}\) is defined as 8π\(^2\)/3

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B_(\text{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-0.1420(1)</td>
<td>0.1033(2)</td>
<td>0.2263(1)</td>
<td>2.23(2)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0006(2)</td>
<td>0.3115(3)</td>
<td>0.3832(2)</td>
<td>2.28(3)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.3351 (9)</td>
<td>0.317(2)</td>
<td>0.1982(9)</td>
<td>3.0(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-0.3189(8)</td>
<td>0.170(1)</td>
<td>0.0880(7)</td>
<td>2.4(1)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-0.2337(9)</td>
<td>0.289(1)</td>
<td>-0.0302(7)</td>
<td>2.5(2)</td>
</tr>
<tr>
<td>O</td>
<td>-0.2241(7)</td>
<td>0.166(1)</td>
<td>-0.1410(6)</td>
<td>3.3(1)</td>
</tr>
</tbody>
</table>
Fig. 1. Part of the \([\text{CuCl}(\text{C}_2\text{H}_5\text{O}))\] polymer showing the atomic numbering. The symmetry code is as for Table 2. Thermal ellipsoids enclose 50% probability.\textsuperscript{11} Hydrogen atoms have been omitted.

The paucity of information available on the monoclinic phase does not, however, permit a detailed comparison of the two structures. In the present compound copper(I) is approximately tetrahedrally coordinated (Fig. 1, Table 2) by two chloride ligands and the \(\text{C}=\text{C}\) double bond and the carbonyl oxygen of two symmetry related acrylaldehyde molecules. The Cu–C coordination distances, 2.075(9) and 2.088(7) \(\text{Å}\), agree well with values determined previously for \(\pi\)-olefinic complexes of copper(I).\textsuperscript{12} The midpoint, \(X\), of the \(\text{C}=\text{C}\) bond is 1.967(8) \(\text{Å}\) from Cu and the X–Cu–O, X–Cu–Cl and X–Cu–Cl\textsuperscript{II} angles are 94.2(3), 121.9(3) and 121.4(2)\textsuperscript{o}, respectively (for

Fig. 2. Stereoscopic view\textsuperscript{11} of the unit cell. All atoms are depicted as spheres: Cu with radius 0.07 \(\text{Å}\); Cl with radius 0.09 \(\text{Å}\); C with radius 0.03 \(\text{Å}\) and O (open circles) with radius 0.055 \(\text{Å}\). The fragment illustrated in Figure 1 is shown at 1+x, y, z.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance ((\text{Å}))</th>
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<tr>
<td>Cu–C(3)</td>
<td>2.075(9)</td>
</tr>
<tr>
<td>Cu–C(2)</td>
<td>2.088(7)</td>
</tr>
<tr>
<td>Cu–Cl</td>
<td>2.289(2)</td>
</tr>
<tr>
<td>Cu–Cl\textsuperscript{II}</td>
<td>2.294(2)</td>
</tr>
<tr>
<td>Cu–O\textsuperscript{I}</td>
<td>2.296(6)</td>
</tr>
<tr>
<td>C(3)–C(2)</td>
<td>3.62(12)</td>
</tr>
<tr>
<td>C(2)–Cl\textsuperscript{I}</td>
<td>1.485(10)</td>
</tr>
<tr>
<td>Cu–Cl\textsuperscript{I}</td>
<td>1.230(9)</td>
</tr>
<tr>
<td>C(3)–Cu–C(2)</td>
<td>38.2(3)</td>
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<td>C(3)–Cu–Cl</td>
<td>91.7(3)</td>
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<td>104.2(3)</td>
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<td>C(3)–Cu–Cl\textsuperscript{II}</td>
<td>104.6(2)</td>
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<td>C(2)–Cu–O\textsuperscript{I}</td>
<td>50.0(2)</td>
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<td>C(2)–Cu–Cl\textsuperscript{I}</td>
<td>119.0(6)</td>
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<tr>
<td>C(2)–Cu–Cl\textsuperscript{II}</td>
<td>109.09(7)</td>
</tr>
<tr>
<td>C(2)–Cu–Cl\textsuperscript{III}</td>
<td>71.4(5)</td>
</tr>
</tbody>
</table>
symmetry code see Table 2). The ligand tetra-
hedron thus exhibits trigonal pyramidal distor-
sion such that copper(I) lies 0.270(4) Å from
the plane through Cl, Cl' and X.

Owing to the low precision associated with the
positions of the hydrogen atoms, it is not mean-
ingful to speculate on the bending back of these
substituents on the basis of torsion angles about
C=C.13 The Cu–C(3)–C(2)–C(1) torsion angle,
−93.6(7)°, would, however, appear to indicate a
slight bending back of the carbonyl carbon
atom.

Apart from a minor decrease in the C(1)–
C(2)–C(3) angle, the connectivity relationships
within the acrylaldehyde ligand do not differ
from those determined by electron diffraction14
or from the microwave spectrum of s-trans acryl-
aldehyde per se.15 Insignificant or very slight
lengthening of the C=C bond has been observed
in several other π-olefinic complexes of cop-
pper(I), e.g. ref. 12b, c, e, g–i and has been inter-
preted as suggesting that the ligand → metal
component is the dominant contribution to the
olefin-copper(I) bond.

Complexes containing acrylaldehyde as a li-
gand have been isolated for rhodium(I),16 and for
zerovallent nickel,17 iron18 and molybdenum.19 In
the iron complex acrylaldehyde is considered to
be coordinated solely via C=C; for the com-
plexes with nickel(0) alternative structures with
and without the participation of the carbonyl
group are discussed.17 In [Mo(C5H5)2(CO)2],
acrylaldehyde is considered to bridge adjacent
molybdenum atoms via π-complexation involving
both C=C and C=O.19 The IR spectrum of the
rhodium(I) complex indicates the presence of
two different acrylaldehyde ligands, one acting as
a bridge via C=C and C=O and the other coor-
nated solely through C=C.16

In the present π-complex, acrylaldehyde also
coordinates copper(I) through the carbonyl oxy-
gen (cf also ref. 5), presumably via a lone-pair
rather than via π(CO) donation [C(1)···Cu = 3.334(7) Å]. The copper(I)-oxygen distance, 2.296(6) Å, is close to that found in bis (triphe-
nylphosphine)copper(I) nitrate, viz. 2.22(1) Å,20
but longer than the copper(I)-oxygen distances
involving the μ-benoato ligands in [CuL(tmen)2
(μ-PhCO2)](μ-CO)[(BPh4) and [CuL(tmnp)2(μ-
PhCO2)](μ-CO)[(BPh4), which range from
1.972(4) to 2.011(6) Å.21 [tmen = N, N, N', N'-
tetramethylethylenediamine; tmnp = N, N, N', N'-
tetramethylpropylenediamine].

The C=O bond length in chloro[2-3-η-(prop-2-
en-1-al)] copper(I), 1.230(9) Å, is comparable to
those within the μ-benoato ligands in the above-
mentioned compounds.21 The acrylaldehyde
ligand is not appreciably distorted from planarity
on coordination, the C(3)–C(2)–Cu–O torsion
angle being −172(1)°. The copper atom, Cu",
bonded to O lies 0.86(3) Å from the least-squares
plane through the ligand and the C(2)–C(1)−
O–Cu" torsion angle is 27(1)° (for symmetry code
see Table 2). The Cu–Cl bridging distances and
the Cu–Cl–Cu angle (Table 2) are typical of those
determined for analogous μ-chloro complexes of
copper(I).12 There are no Cu···Cu contacts less
than 3.733(2) Å.

The connectivity relationships within the
bridging acrylaldehyde molecule, the retention of
the s-trans conformation and the approximate
planarity of the ligand suggest that both the
olefin-copper(I) and the oxygen-copper(I) inter-
actions are relatively weak. This is in accord-
ance with vapour pressure data4 for crystalline [CuCl2-
(C5H5)2] and with the rapid loss of acrylaldehyde
on exposure of the compound to the atmosphere.
Participation of the carbonyl oxygen atom in co-
ordination, which is also thought to occur in π-
intermediates between lithium organocuprates(I)
and α,β-unsaturated carbonyl compounds, might
be expected to result in a weakening of the olefin
→ metal component and a concomitant strength-
ening of the metal → olefin component of the
copper(I)-olefin bond. Both the olefin → metal
and the metal → olefin components could be
expected to be associated with a slightly stronger
interaction involving the β-carbon atom. In the
present study, however, Cu–C(2) and Cu–C(3)
distances cannot be considered to differ.

Acknowledgements. Financial support from the
Swedish Natural Science Research Council (NFR) and from the National Swedish Board for
Technical Development (STU) is gratefully ac-
nowledged.

References


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Received July 5, 1985.