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

Staffan Andersson,[a] Mikael Håkansson,[a] Susan Jagner,*[a] Martin Nilsson,*[b] Christina Ullenius[b] and Fabio Urso[b]

[a]Department of Inorganic Chemistry and [b]Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

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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 (Mo$K\alpha$) diffractometer data. [$CuCl(C_3H_4O)$] crystallizes in space group $P2_12_12_1$ 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 [$I > 3.0\ \sigma(I)$] 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–C 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,[1] and, in particular, selective conjugate addition.[2] 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 ^{13}C NMR spectra.[3] 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.[4] 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 $P2_1/c$ 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.[5]

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[6] 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

*To whom correspondence should be addressed.

providing circulation of ethanol at −20 °C, approximately 10 ml acrylaldehyde 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 acrylaldehyde under nitrogen. Crystals of [CuCl(C$_3$H$_4$O)] decompose losing acrylaldehyde within seconds of exposure to air.

Crystals of chloro[2-3-η-(prop-2-en-1-al)] copper(I), [CuCl(C$_3$H$_4$O)], M_r = 155.1, are orthorhombic, space group $P2_12_12_1$, a = 8.722(4), b = 5.508(2), c = 9.828(4) Å, Z = 4, D_c = 2.18 g cm^{-3}, μ(Mo$K\alpha$) = 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 $P2_1$ diffractometer using graphite-monochromated Mo$K\alpha$ 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 $I > 3.0\ \sigma(I)$ 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 polarisation 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 $I < 3.0\ \sigma(I)$ reflections at their measured values, was 0.057. Atomic scattering factors were taken from ref. 9 and the F_o values were weighted according to $w = [\sigma^2(F_o) + 0.0095F_o^2]^{-1}$. 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-al)]copper(I), adjacent copper(I) atoms are bridged by acrylaldehyde, 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;[5] the

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in [CuCl(C$_3$H$_4$O)]. B_{eq} is defined as $8\pi^2/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{eq}
Cu	−0.1420(1)	0.1033(2)	0.2263(1)	2.23(2)
Cl	0.0006(2)	0.3115(3)	0.3832(2)	2.28(3)
C(3)	−0.3351 (9)	0.317(2)	0.1982(9)	3.0(2)
C(2)	−0.3189(8)	0.170(1)	0.0880(7)	2.4(1)
C(1)	−0.2337(9)	0.269(1)	−0.0302(7)	2.5(2)
O	−0.2241(7)	0.166(1)	−0.1410(6)	3.3(1)

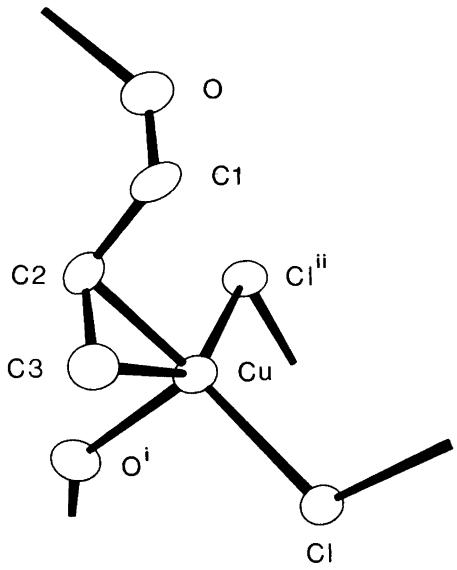

Fig. 1. Part of the $[CuCl(C_3H_4O)]$ polymer showing the atomic numbering. The symmetry code is as for Table 2. Thermal ellipsoids enclose 50 % probability.[11] Hydrogen atoms have been omitted.

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 C=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) Å, agree well with values determined previously for π-olefinic complexes of copper(I).[12] The midpoint, X, of the C=C bond is 1.967(8) Å from Cu and the X–Cu–O^i, X–Cu–Cl and X–Cu–Cl^{ii} angles are 94.2(3), 121.9(3) and 121.4(2)°, respectively (for

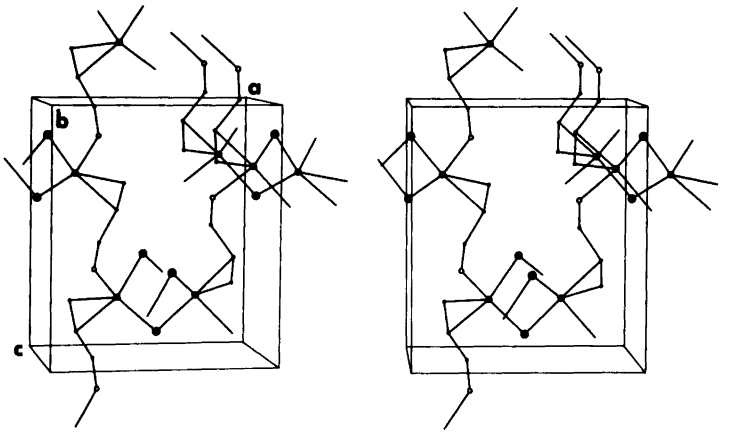

Fig. 2. Stereoscopic view[11] of the unit cell. All atoms are depicted as spheres: Cu with radius 0.07 Å; Cl with radius 0.09 Å; C with radius 0.03 Å and O (open circles) with radius 0.055 Å. The fragment illustrated in Figure 1 is shown at $1+x, y, z$.

Table 2. Interatomic distances (Å) and angles (°) involving the non-hydrogen atoms in chloro[2-3-η-(prop-2-en-1-al)]copper(I). Symmetry code: (*i*): $\bar{x}-\frac{1}{2}, \bar{y}, \frac{1}{2}+z$; (*ii*): $\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$; (*iii*): $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; (*iv*): $\bar{x}-\frac{1}{2}, \bar{y}, z-\frac{1}{2}$.

Cu–C(3)	2.075(9)	Cu–Cl	2.289(2)	C(2)–C(1)	1.485(10)
Cu–C(2)	2.088(7)	Cu–Cl^{ii}	2.294(2)	C(1)–O	1.230(9)
Cu–O^i	2.296(6)	C(3)–C(2)	1.362(12)		
C(3)–Cu–C(2)	38.2(3)	C(2)–Cu–Cl^{ii}	102.4(2)	Cu–C(2)–C(3)	70.4(5)
C(3)–Cu–O^i	91.7(3)	O^i–Cu–Cl	102.6(2)	Cu–C(2)–C(1)	101.8(5)
C(3)–Cu–Cl	104.2(3)	O^i–Cu–Cl^{ii}	95.0(2)	C(3)–C(2)–C(1)	117.0(7)
C(3)–Cu–Cl^{ii}	140.6(2)	Cl–Cu–Cl^{ii}	112.03(6)	C(2)–C(1)–O	123.8(7)
C(2)–Cu–O^i	96.1(3)	Cu–Cl–Cu^{iii}	109.09(7)	C(1)–O–Cu^{iv}	140.0(6)
C(2)–Cu–Cl	138.8(2)	Cu–C(3)–C(2)	71.4(5)		

symmetry code see Table 2). The ligand tetrahedron thus exhibits trigonal pyramidal distortion such that copper(I) lies 0.270(4) Å from the plane through Cl, Cl^{ii} and X.

Owing to the low precision associated with the positions of the hydrogen atoms, it is not meaningful 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[13b] 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 diffraction[14] or from the microwave spectrum of *s-trans* acrylaldehyde *per se*.[15] Insignificant or very slight lengthening of the C=C bond has been observed in several other π-olefinic complexes of copper(I), *e.g.* ref. 12b, c, e, g–i and has been interpreted [12i] as suggesting that the ligand → metal component is the dominant contribution to the olefin-copper(I) bond.

Complexes containing acrylaldehyde as a ligand have been isolated for rhodium(I),[16] and for zerovalent nickel,[17] iron[18] and molybdenum.[19] In the iron complex acrylaldehyde is considered to be coordinated solely *via* C=C;[18] for the complexes with nickel(0) alternative structures with and without the participation of the carbonyl group are discussed.[17] In [Mo(C_3H_4O)$_2$(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 coordinated solely through C=C.[16]

In the present π-complex, acrylaldehyde also coordinates copper(I) through the carbonyl oxygen (*cf* also ref. 5), presumably *via* a lone-pair rather than *via* π(CO) donation [C(1)···Cu^{iv} = 3.334(7) Å]. The copper(I)-oxygen distance, 2.296(6) Å, is close to that found in bis (triphenylphosphine)copper(I) nitrate, *viz.* 2.22(1) Å,[20] but longer than the copper(I)-oxygen distances involving the μ-benzoato ligands in [Cu$_2$(tmen)$_2$(μ–PhCO$_2$)(μ–CO)](BPh)$_4$ and [Cu$_2$(tmpn)$_2$(μ–PhCO$_2$)(μ–CO)](BPh$_4$), which range from 1.972(4) to 2.011(6) Å,[21] [tmen = N, N, N′, N′-tetramethylethylenediamine; tmpn = 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-benzoato ligands in the above-mentioned compounds.[21] The acrylaldehyde ligand is not appreciably distorted from planarity on coordination, the C(3)–C(2)–C(1)–O torsion angle being −172(1)°. The copper atom, Cu^{iv}, bonded to O lies 0.86(3) Å from the least-squares plane through the ligand and the C(2)–C(1)–O–Cu^{iv} 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) interactions are relatively weak. This is in accordance with vapour pressure data[4] for crystalline [CuCl(C_3H_4O)] and with the rapid loss of acrylaldehyde on exposure of the compound to the atmosphere. Participation of the carbonyl oxygen atom in coordination, 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 strengthening 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.

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