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Synthesis and structure of a polymeric complex between methyl acrylate and copper(I) chloride

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Abstract

Chloro[2,3-η-(methyl propenoate)]copper(I) has been prepared by reaction between methyl acrylate and copper(I) chloride, previously activated by formation and subsequent decomposition of a tetrameric π-complex with methyl vinyl ketone. The compound dissociates completely into its constituents, CuCl(s) and methyl acrylate, at temperatures above 0 °C. Its structure has been determined from single-crystal X-ray diffraction data recorded at −105 °C. $[CuCl(C_4H_6O_2)]$, $M_r = 185.1$, crystallizes in space group $C2/c$ with a 14.625(6), b 7.108(3), c 11.681(5) Å, β 93.64(4)° and $Z = 8$. Full-matrix least-squares refinement of 91 structural parameters gave $R = 0.048$ for 1159 observed ($I > 3\sigma(I)$) reflections. The copper is approximately tetrahedrally coordinated by two chloride ligands, the C=C of one methyl acrylate ligand, and the carbonyl oxygen of another such ligand. The structure can be described in terms of $(CuCl)_2$ dimers bridged by methyl acrylate ligands to form layers in the b–c plane. The ligand tetrahedron exhibits trigonal pyramidal distortion such that copper(I) lies 0.386(3) Å from the plane through the two chloride ligands and the midpoint of the C=C bond. The Cu–C distances are 2.035(6) and 2.067(5) Å, C=C 1.370(8) Å and Cu–O 2.288(4) Å. The methyl acrylate ligand exhibits the *s-trans* conformation and the skeleton of the molecule deviates slightly from planarity.

Introduction

In π-complexes between α,β-unsaturated carbonyl compounds and copper(I) chloride the conformation of the ligand has been found to vary, in some cases, assuming a conformation differing from the preferred conformation of the free ligand. In the acrylaldehyde complex [1], the ligand retains the preferred [2–5] *s-trans* conformation and bridges adjacent copper(I) atoms via the C=C bond and the carbonyl oxygen [1]. In the tetrameric complex formed between methyl vinyl ketone and copper(I) chloride [6], there are two types of butenone ligand: one bridging, with the preferred [5,7] *s-trans* conformation, and one terminal, with the *s-cis* conformation, bonded to copper(I) solely via C=C [6]. On complexation with copper(I) chloride, ethyl vinyl ketone assumes the *s-cis* conformation exclusively, bridging adjacent copper(I) atoms via C=C and via a relatively weak interaction involving the carbonyl oxygen (O–Cu = 2.606(6) Å) [8], although the *s-trans* conformer of 1-penten-3-one is the more stable in the uncomplexed state [5]. This may indicate a relationship between the preference for coordination to copper(I) via the C=C double bond rather than the carbonyl oxygen and the conformation of the ligand in the resulting complex. Unlike acrylaldehyde, the minimum energy conformation for uncomplexed methyl acrylate is *s-cis* (see ref. 9 and references therein). The present investigation was undertaken in an attempt to prepare a π-complex between copper(I) chloride and methyl acrylate, and to find out whether or not the methyl acrylate ligand retains the *s-cis* conformation in such a complex.

Experimental

All operations were carried out under nitrogen or argon by Schlenk techniques. Methyl vinyl ketone (Fluka pract.) and methyl acrylate (Merck) were dried with 3 Å molecular sieves and were distilled and deoxygenated, care being taken to avoid polymerisation. Copper(I) chloride was purified as described in ref. 10, and dried under reduced pressure.

Activation of copper(I) chloride with methyl vinyl ketone

10 mmol copper(I) chloride was dissolved in 10 ml methyl vinyl ketone at ca. −50 °C. The solution was allowed to warm slowly, with vigorous stirring, to ambient temperature (but below 27 °C; i.e. the maximum temperature at which $[Cu_4Cl_4(C_4H_6O)_4]$ can exist), a yellow microcrystalline precipitate of $[Cu_4Cl_4(C_4H_6O)_4]$ [6] being obtained. The mother-liquor was removed by filtering or with a syringe, and the precipitate was slowly decomposed by pumping off the butenone ligand at a temperature slightly above 27 °C.

Preparation of chloro[2,3-η-(methyl propenoate)]copper(I)

Approximately 10 ml of methyl acrylate was distilled into one of the legs of an H-type Schlenk tube containing 5 mmol copper(I) chloride, previously activated by complexation with methyl vinyl ketone. The mixture was stirred vigorously at −78 °C until a pale yellow precipitate had been formed (approximately 30 min). Slow evaporation was attained by maintaining the leg containing the unfiltered solution at −25 °C and the other leg of the Schlenk at −196 °C, and pale-yellow crystals of $[CuCl(C_4H_6O_2)]$ were deposited from the solution after a few weeks.

The maximum temperature, T_{max}, at which the complex between copper(I) chloride and methyl vinyl ketone can exist was determined by gradual warming of a mixture of crystals and mother-liquor in a sealed Schlenk tube in a thermostatically controlled bath. $[Cu_4Cl_4(C_4H_6O)_4]$ was found to dissociate completely into copper(I) chloride and methyl vinyl ketone at 27 °C. Similar studies on $[CuCl(C_4H_6O_2)]$ gave a value of T_{max} of 0 °C for this compound.

Crystal and intensity data

$C_4H_6ClCuO_2$, $M_r = 185.1$, monoclinic, space group $C2/c$ (No. 15) [11], a 14.625(6), b 7.108(3), c 11.681(5) Å, β 93.64(4)°, $Z = 8$, D_c 2.03 g cm^{-3}, μ(Mo-K_α) 4.07 mm^{-1}.

A crystal with the approximate dimensions 0.20 × 0.45 × 0.30 mm, was mounted in a glass capillary, containing argon, at −110 °C and transferred to a Syntex $P2_1$ diffractometer, care being take to keep the temperature of the capillary and its contents below −100 °C. Intensity data were measured at −105 °C for $3.5 < 2\theta < 55.0°$ using graphite-monochromated Mo-K_α radiation and the ω–2θ scan mode with a variable 2θ scan rate of 3.0–29.3 min^{-1}. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method [12] was used to calculate the intensities [13]. Of the 1398 independent reflections measured, excluding those systematically absent, 1159 had $I > 3\sigma(I)$, and were considered observed. Unit-cell dimensions were determined from diffractometer setting angles for 15 reflections.

Structure determination and refinement

The positions of the copper(I), chlorine and one of the oxygen atoms were obtained by direct methods (MITHRIL) [14] and the remaining atoms were located from an electron-density map. Full-matrix least-squares refinement of positional and isotropic thermal parameters for the non-hydrogen atoms gave an R value of 0.10; after an empirical correction for the effects of absorption [15], R was reduced to 0.064. Inclusion of anisotropic thermal parameters ($R = 0.054$), and, finally of positional parameters for the hydrogen atoms, located from a difference map, gave a final R value of 0.048 for 91 parameters and 1159 reflections. The isotropic thermal parameters of the hydrogen atoms were set equal to the B_{eq} values of the carrying carbon atoms and not refined. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [11] and the F_o values were weighted according to $w = [\sigma^2(F_o + 0.00001F_o^2]^{-1}$, $R_w = 0.056$. The final difference map had a maximum residual electron density of 1.2 e Å^{-3}. The computer programs used were as described in refs. 16 and 17 and the figure was drawn by use of the ORTEP program [18]. Fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1 and interatomic

Table 1

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in chloro[2,3-η-methyl propenoate)]copper(I) [a]

Atom	x	y	z	B_{eq}
Cu	0.21921(5)	0.23557(8)	0.12066(5)	1.89(2)
Cl	0.2831(1)	0.4805(2)	0.0225(1)	2.21(3)
C(1)	0.0296(5)	0.7127(9)	0.0886(6)	2.9(2)
O(1)	0.0547(3)	0.5312(5)	0.1359(3)	2.1(1)
C(2)	0.1206(4)	0.5317(7)	0.2197(4)	1.9(1)
O(2)	0.1535(3)	0.6731(5)	0.2614(3)	2.2(1)
C(3)	0.1504(4)	0.3406(8)	0.2560(4)	2.2(1)
C(4)	0.1107(4)	0.1770(8)	0.2155(4)	2.1(1)

[a] B_{eq} is defined $(8\pi^2)/3\ \Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star\ \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 2

Interatomic distances and angles involving the non-hydrogen atoms in chloro[2,3-η-(methyl propenoate)]copper(I) [a]

Cu–X	1.933(6)	C(1)–O(1)	1.442(7)
Cu–C(3)	2.067(5)	O(1)–C(2)	1.329(6)
Cu–C(4)	2.035(6)	C(2)–O(2)	1.204(6)
Cu–Cl	2.314(2)	C(2)–C(3)	1.480(8)
Cu–Cl^{i}	2.269(2)	C(3)–C(4)	1.370(8)
Cu–O^{ii}	2.288(4)	Cu ··· Cu^{i}	3.020(2)
X–Cu–Cl	126.2(2)	C(1)–O(1)–C(2)	115.8(4)
X–Cu–Cl^{i}	126.2(2)	O(1)–C(2)–O(2)	123.5(5)
X–Cu–O^{ii}	98.9(2)	O(1)–C(2)–C(3)	113.3(4)
Cl–Cu–Cl^{i}	97.55(6)	O(2)–C(2)–C(3)	123.2(5)
Cl–Cu–O^{ii}	96.1(1)	C(2)–C(3)–C(4)	124.7(5)
Cl^{i}–Cu–O^{ii}	106.6(1)	C(2)–O(2)–Cu^{iii}	134.0(4)
Cu–Cl–Cu^{i}	82.45(6)		

[a] X is the midpoint of the C(3)–C(4) bond. Estimated standard deviations are given in parentheses. Symmetry code: (i); $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ii): $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii): $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$. The C–H bond distances lie in the range 0.72(9)–1.05(8) Å.

distances and angles involving the non-hydrogen atoms in Table 2. Lists of observed and calculated structure factors, fractional coordinates 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

It has been demonstrated that complexes between copper(I) chloride and olefins can only be formed at temperatures less than a maximum reaction temperature at which the dissociation pressure is equal to the vapour pressure of the free ligand [19]. π-Complexes between copper(I) chloride and α,β-unsaturated carbonyl compounds are likewise unstable with respect to loss of the organic ligand [1,6,8,20], and the difference in the maximum reaction temperatures, $T_{\max}$, for the butenone and methyl propenoate complexes has been exploited in the preparation of chloro[2,3-η-(methyl propenoate)]copper(I). The low value of $T_{\max}$ for the latter compound (approximately 0 °C) results in an extremely slow direct reaction between methyl acrylate and copper(I) chloride, crystals of the compound being obtained after a period of 6 months to one year. If copper(I) chloride is activated by formation and subsequent dissociation of the complex with methyl vinyl ketone, prior to exposure to methyl acrylate, the reaction can be made to proceed at an acceptable rate.

In chloro[2,3-η-(methyl propenoate)]copper(I), the methyl acrylate ligand assumes the *s-trans* conformation, bridging $(CuCl)_2$ dimers to form layers (Fig. 1), bounded by the methyl groups, interlayer contacts thus being of van der Waals order. The skeleton of the methyl acrylate ligand shows slight deviation from planarity (Table 3). As in the acrylaldehyde [1], butenone [6], pentenone [8] and acrylic acid [21] analogues, and in many other π-olefinic complexes of copper(I) (see e.g. ref. 1 and references therein) the C=C bond is only marginally lengthened on coordination. The values determined for C=C in monomeric methyl acrylate in the

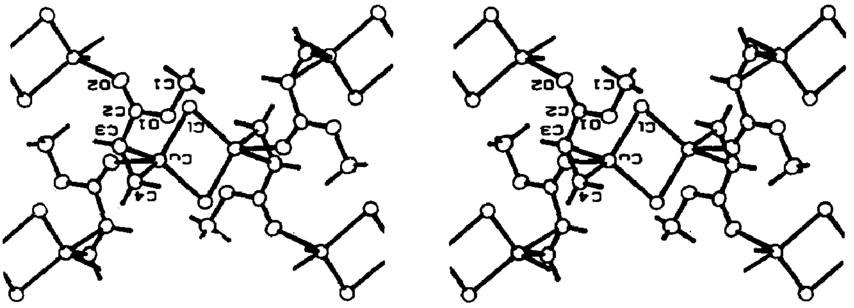

Fig. 1. Stereoscopic view of $[CuCl(C_4H_6O_2)]$. The thermal ellipsoids enclose 50% probability.

crystalline [22] and liquid [23] states are 1.34(2) and 1.36 Å, respectively. The remaining bond distances and angles within the ligand (Table 2) are all also in good agreement with those determined for the uncomplexed molecule [22,23].

Copper(I) is four-coordinated by two chloride ligands, the C=C bond of one methyl acrylate ligand, and the carbonyl oxygen of another, the coordination polyhedron exhibiting trigonal pyramidal distortion such that the copper(I) atom lies 0.386(3) Å from the plane through the two chloride ligands and X, the midpoint of the C=C bond. The corresponding displacement in the acrylaldehyde analogue is 0.270(4) Å [1]. The olefin is symmetrically positioned with respect to the chloride ligands in the trigonal plane, and there is no evidence for sliding of the olefin group [24]. The Cu–C(4)–C(3)–C(2) torsion angle, 94.4(6)°, appears to indicate [24] a slight bending back of the carbonyl carbon atom, but owing to the low precision in the positions of the hydrogen atoms it is not possible to decide solely on the basis of the torsion angles about C=C (Table 3) whether or not these substituents are bent back. The Cu–C distances, 2.035(6) and 2.067(5) Å hardly differ (5σ), and both these distances and the Cu–O bond length are closely similar to the corresponding distances determined for the complex with acrylaldehyde. The Cu–C(olefin) distances in the complex between acrylic acid and copper(I) chloride are 2.040(7) and 2.043(8) Å, respectively [21]; in that compound the coordination to copper(I) is solely via C=C, the carboxyl groups giving rise to hydrogen-bonded dimers which each bridge two copper(I) centres.

Cu^{iii} lies 0.384(8) Å from the least-squares plane through the skeleton of the methyl acrylate ligand and the C(3)–C(2)–O(2)–Cu^{iii} torsion angle is 12.3(6)° (for symmetry code see Table 3). Corresponding values for the acrylaldehyde complex are 0.86(3) Å and 27(1)° [1].

Table 3

Selected torsion angles (°) in chloro[2,3-η-(methyl propenoate)]copper(I) [a]

Cu–C(4)–C(3)–C(2)	94.4(6)	C(1)–O(1)–C(2)–O(2)	5.7(7)
Cu–C(4)–C(3)–H(3)	−88(5)	C(1)–O(1)–C(2)–C(3)	−173.7(6)
Cu–C(3)–C(4)–H(4A)	−94(5)	O(1)–C(2)–C(3)–C(4)	−4.8(7)
Cu–C(3)–C(4)–H(4B)	95(6)	O(2)–C(2)–C(3)–C(4)	175.7(8)
		C(3)–C(2)–O(2)–Cu^{iii}	12.3(6)

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

Table 4

Copper(I)–olefin, oxygen–copper(I) distances (Å) and ligand conformations in some complexes between copper(I) chloride and α,β-unsaturated carbonyl compounds

	Complex between copper(I) chloride and				
	acrylaldehyde [a]	methylacrylate [b]	methyl vinyl ketone [c]		ethyl vinyl ketone [d]
			bridging	terminal	
Cu–C(olefin)	2.075(9)	2.035(6)	2.10(2)	2.07(2)	2.048(6)
	2.088(7)	2.067(5)	2.07(2)	2.10(2)	2.060(6)
O–Cu	2.296(6)	2.288(4)	2.33(2)	–	2.606(6)
Ligand conformation	*s-trans*	*s-trans*	*s-trans*	*s-cis*	*s-cis*
Preferred conformation of uncomplexed ligand	*s-trans* [e]	*s-cis* [f]	*s-trans* [g]	*s-trans* [g]	*s-trans* [h]

[a] Ref. 1. [b] This work. [c] Ref. 6. [d] Ref. 8. [e] Refs. 2–5. [f] Ref. 9 and references therein. [g] Ref. 5, 7. [h] Ref. 5.

Although the preferred conformation of methyl acrylate per se is *s-cis*, that of the ligand in the present complex is *s-trans*, presumably owing to the relatively strong O–Cu interaction in addition to coordination to copper(I) via the olefinic group. The ligand conformations, and Cu–C(olefin) and O–Cu distances in the complexes between α,β-unsaturated carbonyl compounds and copper(I) chloride prepared and investigated hitherto are summarised in Table 4.

Methyl acrylate retains the *s-cis* conformation, however, in two complexes in which it is bonded to the metal solely via C=C. Thus (η^2-methyl acrylate)$_2$W(CO)$_4$ contains two methyl acrylate ligands *trans* to one another, both with the *s-cis* conformation [25]. In (1-η^5-cyclopentadienyl)(1,2:1,3-μ-dicarbonyl)(1-η^2;2,3-σ-methyl acrylate)(2,2,2,3,3,3-hexacarbonyl)*triangulo*-1-manganese-2,3-diiron, the methyl acrylate ligand, which σ-bridges two iron atoms, is also π-bonded to manganese [26].The carbonyl oxygen does not participate in coordination, and the conformation of the ligand is approximately *s-cis*, with rotation of the COOMe group with respect to the olefin so that the skeleton of the molecule is no longer planar, the C=C–C=O torsion angle being $-20.9(3)°$ [26].

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