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A tetrameric copper(I) alkoxide with a π-tethered ligand: 2-allyl-6-methylphenoxocopper(I)

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Abstract

The complex 2-allyl-6-methylphenoxocopper(I) has been prepared by reaction between mesitylcopper(I) and 2-allyl-6-methylphenol. Crystallographic studies show that the compound is tetrameric with a distorted cubane-type copper(I)-oxygen core, and with additional π-coordination of the ligand to copper through the alkene functionality (ν(C=C) = 1520 cm^{-1}). The ligands thus act both as chelates and as bridges between adjacent copper(I) centres. Copper(I) exhibits trigonal pyramidal coordination geometry with Cu–C distances to the C=C group of 1.976(9) and 2.017(11) Å and Cu–O distances of 1.973(6), 2.021(6) and 2.577(6) Å, respectively. © 2002 Published by Elsevier Science B.V.

Keywords: Copper(I); Alkene; Alkoxide; Phenoxide; 2-Allyl-6-methylphenol; Infrared spectroscopy; NMR spectroscopy; Crystal structure

1. Introduction

Information concerning structures and properties of homoleptic copper(I) alkoxides is still relatively scarce. Until recently, only a handful of such compounds had been prepared [1–3] and, of these, only the structure of *t*-butoxocopper(I) had been investigated [2]. In recent studies [4,5] evidence for the occurrence of tetranuclear Cu_4O_4-cores in homoleptic copper(I) alkoxides and aryloxides has been provided. Thus, in general, the structures of homoleptic copper(I) alkoxides appear to resemble those of homoleptic arylcopper complexes [6–10], in that they are tetrameric with planar or butterfly-shaped Cu_4O_4- or Cu_4C_4-cores, a notable arylcopper exception being pentameric mesitylcopper [11]. A significant difference between the two classes of tetranuclear compounds would, however, appear to be that built-in π-ancillary groups in aryl ligands do not appear to induce additional coordination to the metal centre—the vinyl group is not coordinated to copper in *o*-vinylphenylcopper [7]—but in alkoxide or aryloxide ligands such built-in groups give rise to new structural motifs by additional π-tethering of the ligand to the metal [12]. Arenethiolates of copper(I) with coordinating *ortho* substituents have been shown to yield a rich variety of structural patterns [13] as have lithium analogues [14].

All the aryl- and aryloxo- or alkoxocopper(I) compounds prepared hitherto, are, with one exception, exceedingly labile and decompose within seconds of exposure to the atmosphere. The one exception is *o*-allylphenoxocopper(I) [12], which is relatively stable, decomposing completely only after a few days of exposure to the atmosphere. We were interested in investigating how substitution in the 6-position of the phenol, to yield a mesityl-type analogue, might affect the stability and structure of the resulting compound, and we here report the preparation and characterisation of a new copper(I) phenoxide: 2-allyl-6-methylphenoxocopper(I).

2. Experimental

2.1. General

All operations were carried out under Ar using standard Schlenk techniques. Copper(I) chloride was purified according to literature methods [15]. Mesityl-

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copper(I) was prepared from copper(I) chloride, 2-bromomesitylene and magnesium according to methods described previously [8,11,16]. 2-Allyl-6-methylphenol was used as purchased (Aldrich 98%). Toluene was distilled from sodium/benzophenone shortly prior to use. Infrared spectra were recorded for the solid in Nujol mull and for the pure ligand, using KBr mull windows and a Perkin–Elmer Spectrum One spectrometer, with a resolution of 4 cm^{-1}, and ten scans.

2.2. Preparation of $[Cu_4(OC_6H_3(CH_3)(CH_2C(H){=}CH_2))_4]$

Mesitylcopper(I) (0.73 mmol; 0.135 g) was dissolved in toluene (4 ml) and excess of 2-allyl-6-methylphenol (2.41 mmol; 0.36 ml) was added slowly with a syringe. The resulting solution was stirred for a few seconds, during which it changed colour from yellow to orange; it was then allowed to stand at ambient temperature, pale-yellow rods of $[Cu_4(OC_6H_3(CH_3)(CH_2C(H){=}CH_2))_4]$ being deposited after 24 h. IR $[Cu_4(OC_6H_3(CH_3)(CH_2C(H){=}CH_2))_4]$: $\nu(C{=}C) = 1520\ \text{cm}^{-1}$. The compound is sparingly soluble in toluene and is relatively stable, decomposing completely only after several hours of exposure to the atmosphere. For $HOC_6H_3(CH_3)(CH_2C(H){=}CH_2)$: $\nu(C{=}C) = 1637\ \text{cm}^{-1}$.

2.3. X-ray crystallography

Crystal and experimental data are summarised in Table 1. A crystal of $[Cu_4(OC_6H_3(CH_3)(CH_2C(H){=}CH_2))_4]$ was mounted under Ar in a glass capillary at −155 °C [17] and transferred in liquid nitrogen to a Rigaku AFC6R diffractometer. Diffracted intensities were measured using graphite-monochromated Mo–K_α ($\lambda = 0.710\ 73$ Å) radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). Data were recorded at −115 °C for $5 < 2\theta < 50°$ from a pale-yellow rod-shaped crystal with approximate dimensions $0.20 \times 0.10 \times 0.10$ mm, using the ω–2θ scan mode with an ω scan rate of $8°\ \text{min}^{-1}$ and a scan width of $(0.94 + 0.30 \tan\theta)°$. Stationary background counts were recorded on each side of a reflection, the ratio of peak counting time to background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability during the diffraction experiment. Cell constants were obtained by least-squares refinement from the setting angles of 20 reflections. Correction was made for Lorentz and polarisation effects. No correction was made for the effects of absorption owing to lack of suitable reflections for which azimuthal scans could be collected. A total of 871 unique data were thus measured for h, k, l with $h > k$, yielding index ranges of $0 < h < 15$, $0 < k < 11$ and $0 < l < 11$. The structure was solved by direct methods (SIR92 [18]) and refined using full-matrix least-squares calculations on F^2 (SHELXL97 [19]) operating in the WINGX programme package [20]. Anisotropic thermal displacement parameters were refined for all the non-hydrogen atoms and the hydrogen atoms associated with the phenyl ring and the methylene group were included using the riding model. Those associated with the methyl and allyl groups were located from a difference map and refined with isotropic thermal parameters. Refinement of 133 parameters based on all 871 reflections yielded $R_1 = 0.034$ and $wR_2 = 0.078$ for $I > 2\sigma(I)$ and $R_1 = 0.090$ and $wR_2 = 0.098$ for all reflections; maximum and minimum residual electron density: 0.37; −0.54 e Å^{-3}. The Flack absolute structure parameter was −0.02(6). The structural illustration (Fig. 1) has been drawn with ORTEP-3 for Windows [21]. Selected interatomic distances and angles are given in Table 2.

Table 1
Crystallographic data and structure refinement parameters for $[Cu_4(OC_6H_3(CH_3)(CH_2C(H){=}CH_2))_4]$

Empirical formula	$C_{40}H_{44}O_4Cu_4$
M_r	843.0
Crystal system	Tetragonal
Space group	$P\bar{4}2_1c$ (No. 114)
Unit cell dimensions	
a (Å)	13.084(2)
c (Å)	9.956(1)
V (Å^3)	1704(1)
Z	2
F(000)	864
D_{calc} (g cm^{-3})	1.64
μ (Mo–K_α) (cm^{-1})	25.0
T (°C) (data collection)	−115
No. unique data	871
No. with $I > 2.0\sigma(I)$	570
No. parameters refined	133
R_1 ($I > 2.0\sigma(I)$)	0.034
wR_2 ($I > 2.0\sigma(I)$)	0.078
R_1 (all data)	0.090
wR_2 (all data)	0.098
Flack parameter	−0.02(6)
Max/min residual electron density (e Å^{-3})	0.37 and −0.54

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [(\Sigma w(|F_o| - \Sigma|F_c|\Sigma)^2/\Sigma w F_o^2)]^{1/2}$.

2.4. NMR spectroscopy

^{1}H-NMR spectra (500 MHz) for the copper(I) complex dissolved in THF were recorded using a Varian Inova 500 NMR spectrometer and a ^{1}H-NMR spectrum (400 MHz) for the ligand were recorded using a Varian XL 400 spectrometer. (s = singlet, d = doublet, dd = doublet of doublets, ddt = doublet of doublet of triplets, t = triplet, m = multiplet, b = broad). For a solution of 2-allyl-6-methylphenoxocopper(I) in THF,

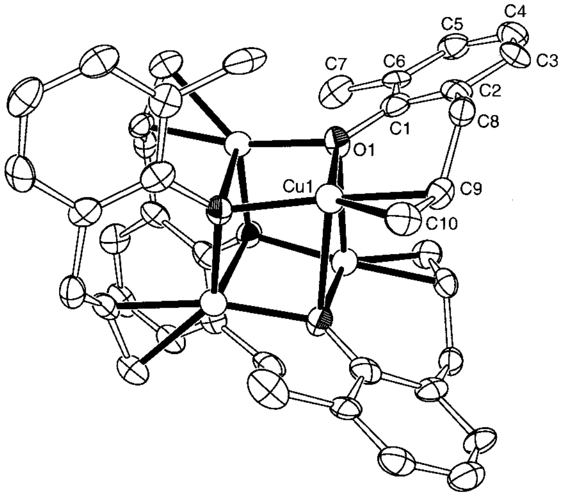

Fig. 1. The $[\mathrm{Cu_4(OC_6H_3(CH_3)(CH_2C(H){=}CH_2))_4}]$ entity showing the crystallographic numbering. The copper(I) coordination sphere, including the cubane-type $\mathrm{Cu_4O_4}$-core, is illustrated by means of filled bonds. Thermal ellipsoids enclose 50% probability.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[\mathrm{Cu_4(OC_6H_3(CH_3)(CH_2C(H){=}CH_2))_4}]$

Bond lengths			
Cu(1)–O(1)	2.021(6)	C(3)–C(4)	1.38(1)
Cu(1)–O(1$^{\mathrm{i}}$)	1.973(6)	C(4)–C(5)	1.37(1)
Cu–C(10)	2.017(11)	C(5)–C(6)	1.37(1)
Cu–C(9)	1.976(9)	C(6)–C(1)	1.42(1)
Cu–X	1.878	C(6)–C(7)	1.51(2)
Cu–O(1$^{\mathrm{ii}}$)	2.577(6)	C(2)–C(8)	1.51(1)
O(1)–C(1)	1.36(1)	C(8)–C(9)	1.51(1)
C(1)–C(2)	1.40(1)	C(9)–C(10)	1.35(2)
C(2)–C(3)	1.39(1)		
Bond angles			
O(1)–Cu(1)–O(1$^{\mathrm{i}}$)	94.9(2)	O(1)–C(1)–C(6)	119.8(9)
O(1$^{\mathrm{ii}}$)–Cu(1)–O(1$^{\mathrm{i}}$)	79.4(2)	C(2)–C(1)–C(6)	118.5(9)
O(1$^{\mathrm{ii}}$)–Cu(1)–O(1)	92.2(2)	C(1)–C(2)–C(3)	119.1(9)
O(1$^{\mathrm{i}}$)–Cu(1)–C(9)	168.0(3)	C(1)–C(2)–C(8)	123.3(8)
O(1)–Cu(1)–C(9)	96.7(3)	C(3)–C(2)–C(8)	117.5(8)
O(1$^{\mathrm{ii}}$)–Cu(1)–C(9)	103.3(3)	C(2)–C(3)–C(4)	121.5(9)
O(1$^{\mathrm{i}}$)–Cu(1)–C(10)	128.4(4)	C(3)–C(4)–C(5)	119.8(9)
O(1)–Cu(1)–C(10)	135.0(4)	C(4)–C(5)–C(6)	120.9(9)
O(1$^{\mathrm{ii}}$)–Cu(1)–C(10)	105.7(4)	C(5)–C(6)–C(1)	120.1(9)
Cu(1$^{\mathrm{ii}}$)–O(1)–Cu(1$^{\mathrm{iii}}$)	84.3(2)	C(5)–C(6)–C(7)	120.2(9)
Cu(1)–O(1)–Cu(1$^{\mathrm{iii}}$)	101.2(3)	C(1)–C(6)–C(7)	119.7(9)
Cu(1)–O(1)–Cu(1$^{\mathrm{ii}}$)	87.1(2)	C(2)–C(8)–C(9)	116.5(7)
Cu(1)–O(1)–C(1)	124.2(5)	C(8)–C(9)–C(10)	125.5(9)
Cu(1$^{\mathrm{ii}}$)–O(1)–C(1)	106.6(5)	C(8)–C(9)–Cu(1)	104.8(6)
Cu(1$^{\mathrm{iii}}$)–O(1)–C(1)	133.2(6)	C(10)–C(9)–Cu(1)	71.8(6)
O(1)–C(1)–C(2)	121.8(8)	C(9)–C(10)–Cu(1)	68.6(6)

X is the midpoint of the C(9)–C(10) bond. Symmetry code: (i): $-y, x, -z-1$; (ii): $-x, -y, z$; (iii): $y, -x, -z-1$.

^{1}H-NMR spectra (ppm) were recorded at 50 to −50 °C using THF-d_8. For a solution of 2-allyl-6-methylphenol in THF a (400 MHz) ^{1}H-NMR spectrum (ppm) was recorded at 20 °C using THF-d_8.

2-Allyl-6-methylphenoxocopper(I) in THF-d_8 at −50 °C: δ 2.19 (s, 3H, –CH$_3$), 3.33 (d, 2H, –CH$_2$–), 4.98 (dd, 2H, =CH$_2$), 5.97 (ddt, 1H, –CH=), 6.63 (t, 1H, phenyl), 6.88 (dd, 2H, phenyl).

2-Allyl-6-methylphenol in THF-d_8 at 20 °C: δ 2.20 (s, 3H, –CH$_3$), 3.37 (d, 2H, –CH$_2$–), 4.95 (d, 1H, =CH$_2$), 5.00 (d, 1H, =CH$_2$), 5.98 (ddt, 1H, –CH=), 6.65 (dd, 1H, phenyl), 6.90 (dd, 2H, phenyl), 7.15 (s, 1H, –OH).

3. Results and discussion

We have shown previously that the reaction between mesitylcopper(I) and alcohols or phenols is an effective preparatory method for copper(I) alkoxides and phenoxides which are less readily accessible by other routes [4,5,12]. Here we demonstrate a further example utilising this general approach, namely the preparation of 2-allyl-6-methylphenoxocopper(I) from mesitylcopper(I) and 2-allyl-6-methylphenol. This compound is the third such alkoxide in which additional coordination to copper(I) is provided by the alkene functionality of the ligand, the two previous analogues being 2-allylphenoxocopper(I) and 2-methyl-3-buten-2-oxocopper(I) [12].

2-Allyl-6-methylphenoxocopper(I) crystallises as a tetramer (cf. Fig. 1). As is apparent from the figure, the complex has a distorted $\mathrm{Cu_4O_4}$ cubane-type core, the distortion being similar to that exhibited by one of the two possible $\mathrm{Cu_4Cl_4(olefin)_4}$ cubane isomers [22,23], namely that in which pairs of parallel long Cu–Cl bonds are mutually orthogonal. The occurrence of two types of structural isomers with distorted cores, as opposed to a cubane core with regular geometry, is largely attributable to the π^*-acceptor properties of the alkene ligand [23]. 2-Allyl-6-methylphenoxocopper(I) has a very similar structure to its non-methylated analogue [12], the main differences lying in the somewhat less distorted core of the present compound, and the lack of disorder associated with the allyl group. In *o*-allylphenoxocopper(I) [12], the C=C bond could be resolved into two crystallographically different positions, which led to poor precision and unrealistically long C=C bond distances. Here the C=C bond at 1.35(2) Å and the concomitant lowering of ν(C=C) by 117 cm^{-1} are typical of those values determined in π-alkene complexes of copper(I) (see, for example, Refs. [22–24], and references therein). Recently, novel η^2-arene interactions have been shown to result in C=C π-coordination patterns similar to those found in copper(I) alkene complexes [25].

The 2-allyl-6-methylphenoxo ligands act both as O, π(C=C) chelates and as O, π(C=C) bridges between adjacent copper(I) centres (cf. Fig. 1). The coordination geometry of copper(I) in 2-allyl-6-methylphenoxocopper(I) can be described as being trigonal pyramidal with oxygen atoms from two phenoxide ligands and the C=C linkage of the allyl group comprising the trigonal plane. The apex of the pyramid is formed by the oxide of a third ligand leading to a Cu···O contact of 2.577(6) Å, which is shorter than that determined for the non-methylated analogue, viz. 2.785(6) Å [12]. The in-plane Cu–O bonds are 1.973(6) and 2.021(6) Å, respectively, while the Cu–C bonds are 1.976(9) and 2.017(11) Å. Copper is displaced 0.10 Å from the plane through O(1), O(1^{i}) and X (where X is the midpoint of the C(9)–C(10) bond) towards the apical oxygen O(1^{ii}). The olefin is twisted 11° out of this plane such that Cu(1), C(9), C(10) and O(1^{i}) are approximately co-planar (r.m.s. deviation from least-squares plane $= 0.004$ Å), indicating a 'quasidodecahedral' olefin twist [26]. Moreover, the asymmetry between the O(1)–Cu(1)–X and O(1^{i})–Cu(1)–X angles (116 and 148°, respectively) indicate appreciable olefin sliding [26b]. The copper(I) centre is not involved in any short Cu···H interactions with the methyl group of an adjacent ligand. Initial refinement in which all the hydrogen atoms were included in calculated positions suggested that a short Cu···H distance might be present, but this was refuted by location of the hydrogen atoms from a difference map and refinement of hydrogen-atom parameters as described above. As mentioned earlier, the allyl group in *o*-allylphenoxocopper(I) is disordered. It is not clear if the methyl substituent is instrumental in inducing order into the allyl group in the present compound.

To gain further insight into the stability of the complex in solution, and for comparison with the non-methylated analogue [12], a ^{1}H-NMR investigation in the temperature interval -50 to $+50$ °C was carried out in THF-d_8. The spectra show clear and distinct signals for all protons on the ligand throughout the whole temperature interval. Upon cooling of the THF solution, minor shift changes are observed but not the characteristic upfield shifts that are typical for olefinic protons upon alkene–copper(I) coordination [27,28]. Thus, it would appear that copper(I)–alkene coordination is not retained in THF. The difference in behaviour in THF in comparison with the non-methylated analogue, *o*-allyl-phenoxocopper(I) [12] is surprising, and it would seem that the methyl group has a de-protecting rather than a protecting effect with respect to attack by THF. It is conceivable that the resulting species is an open planar or butterfly-shaped tetramer of the type observed previously in the solid state [4,5] and also inferred in solution [4,5]. It is also possible that there is additional coordination to copper by THF. Species of lower nuclearity, such as those demonstrated to exist in solutions of related tetrameric zinc aryloxide complexes [29] cannot, however, be ruled out.

In conclusion, 2-allyl-6-methylphenoxocopper(I) provides a further example of a phenoxide with a cubane-type Cu_4O_4-core. This illustrates the seemingly richer structural diversity of homoleptic alkoxides with built-in tethering π-functionalities as compared with the usual pattern of square Cu_4O_4 or Cu_4C_4-cores found in homoleptic Cu–OR and Cu–R compounds [2,4–10], the latter even including R groups with built-in alkene functionalities, e.g. *o*-vinylphenylcopper [7]. Given the rich structural chemistry of arenethiolates of copper(I) and related metals [13,14], it seems likely that further investigations may provide evidence for other more exotic core types, such as the hexanuclear ribbon-shaped core in 2-methyl-3-buten-oxocopper(I) [12]. The presence of the methyl group in the 6-position yields an additional compound that is considerably less labile than the majority of copper(I) alkoxides and phenoxides investigated hitherto [4,5,12]. It is apparent from Fig. 1 that, in the solid state, the methyl groups shield the Cu_4O_4-core to a certain extent, although this would not appear to be the case in solution.

It would seem that introduction of substituents *ortho* to the oxo-group are not a guarantee, per se, for the isolation of a copper(I) phenoxide, even though some success has been achieved in this respect [4]. We were, for instance, unable to isolate 2,6-dimethylphenoxocopper(I) or 2,6-*t*-butylphenoxocopper(I) from mesitylcopper and the relevant phenol, although the products of the reactions between carbon monoxide, mesitylcopper and 2,6-substituted phenols could be obtained [30]. In addition to providing new types of copper(I)-oxide cores, the presence of an ancillary tethering π-functionality in the phenoxo ligand is undoubtedly an important stabilising factor.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 164429. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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