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Copper(II) is harder than copper(I): a novel mixed-valence example from alkoxide chemistry

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Partial oxidation or disproportionation of tetrameric 2-allyl-6-methylphenoxocopper(I) leads to the formation of a novel trinuclear mixed-valence Cu(I)/Cu(II) alkoxide: [Cu₃{OC₆H₃(CH₃)[CH₂C(H)=CH₂]}₄], in which the central copper(II) atom is coordinated in a distorted square-planar configuration by four oxide ligands, whereas the peripheral copper(I) centres are each bonded to two C=C linkages and to two oxide ligands in a tetrahedral arrangement.

Copper(I) was recognised early as a soft Lewis acid whereas copper(II) was defined as being borderline.^{1,2} In accordance with the HSAB (hard and soft acids and bases) principle,^{2,3} difficulties have been encountered in, for instance, the preparation and structural characterisation of homoleptic copper(I) alkoxides and phenoxides.⁴ Thus, until recently, only the structure of *t*-butoxocopper(I) had been determined.^{4a} Subsequent studies^{4b,d} provided evidence for the occurrence of tetranuclear Cu₄O₄ cores, which, in general, appear to resemble the Cu₄C₄ cores of homoleptic arylcopper complexes,⁵ in that they are planar or butterfly-shaped. 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 co-ordinated to copper in *o*-vinylphenylcopper^{5b}—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.^{4c,e} Arenethiolates of copper(I) with co-ordinating ortho substituents, on the other hand, have been shown to yield a rich variety of structural patterns^{6a} as have lithium analogues.^{6b}

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),^{4c} which is relatively stable, decomposing completely only after a few days of exposure to the atmosphere. Substitution in the 6-position of the alcohol, to yield a mesityl-type analogue, appears to have a de-protecting rather than a protecting effect on the resulting phenoxide.^{4e} This compound, 2-allyl-6-methylphenoxocopper(I), provides a further example of a phenoxide with a cubane-type Cu₄O₄ core and a π -tethered phenoxide ligand.^{4e} Storage of the crystals and mother liquor of 2-allyl-6-methylphenoxocopper(I) at -80°C yielded unexpectedly a mixed-valence trinuclear Cu(II)/Cu(I) species, the novel structure of which is the subject of this letter.

Tetrakis(2-allyl-6-methylphenoxo)tricopper(I,II), [Cu₃{OC₆H₃(CH₃)[CH₂C(H)=CH₂]}₄], crystallises as the toluene solvate (1). The structure of the mixed-valence phenoxide, showing

the crystallographic numbering, is depicted in Fig. 1 and selected bond distances and angles are given in Table 1. The structural conversion between the tetranuclear cubane and open trinuclear cores is depicted schematically in Scheme 1. The copper(II) centre, crystallographically numbered as Cu(1), is situated on a two-fold axis and is coordinated by four phenoxide oxygen donors in a distorted square-planar arrangement with Cu(1)–O(1) and Cu(1)–O(2) distances of 1.921(8) and 1.950(8) Å, respectively. The dihedral angles between the O(1)–Cu(1)–O(2) and O(1')–Cu(1)–O(2') planes and the O(1)–Cu(1)–O(2') and O(1')–Cu(1)–O(2) planes are 36.8(2)° and 32.4(2)°, respectively (for symmetry code see Table 1), and thus indicate appreciable distortion from ideal square-planar co-ordination geometry. As is seen in Fig. 1, each phenoxide ligand bridges through O(1) and O(2) to a copper(I) centre, resulting in a trinuclear complex. The copper(I) centres are tetrahedrally coordinated by two oxygen and two alkene donors, with Cu(I)–O distances of 2.076(8) and 2.085(8) Å, and Cu(I)–C distances ranging from 2.086(7) to 2.189(8) Å, similar to those determined for the parent copper(I) phenoxide.^{4e} The 2-allyl-6-methylphenoxide ligands thus act as chelating ligands with respect to copper(I) and bridging with

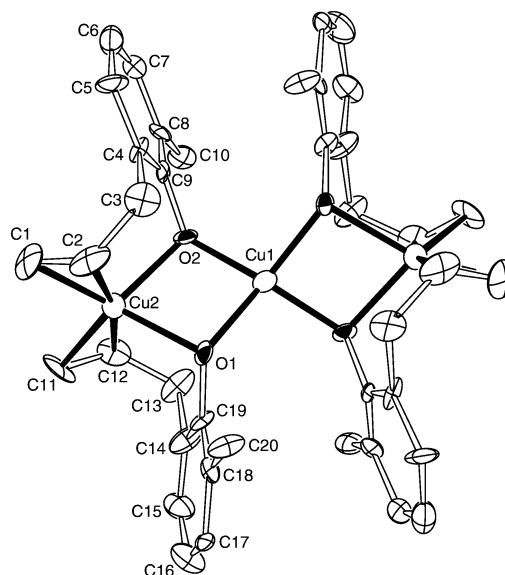


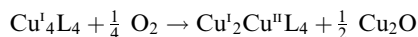
Fig. 1 The structure of [Cu₃{OC₆H₃(CH₃)[CH₂C(H)=CH₂]}₄] showing the crystallographic numbering. Hydrogen atoms have been omitted for clarity. The thermal ellipsoids enclose 50% probability. The two halves of the molecule are related by a two-fold axis through Cu(1), which runs parallel to the crystallographic *b* axis.

Table 1 Selected interatomic distances (Å) and angles (°) for $[\text{Cu}_3\{\text{OC}_6\text{H}_3(\text{CH}_3)[\text{CH}_2\text{C}(\text{H})=\text{CH}_2]\}_4]$. X(1) and X(2) are the mid-points of the C(9)–C(10) and C(19)–C(20) bonds, respectively. Symmetry code: (i): $-x + 2, y, -z + 1/2$

Cu(1)–O(1)	1.921(8)	Cu(2)–O(1)	2.076(8)
Cu(1)–O(2)	1.950(8)	Cu(2)–O(2)	2.085(8)
Cu(2)–C(9)	2.123(6)	Cu(2)–C(19)	2.189(8)
Cu(2)–C(10)	2.126(5)	Cu(2)–C(20)	2.086(7)
Cu(2)–X(1)	2.011	Cu(2)–X(2)	2.028
C(9)–C(10)	1.370(8)	C(19)–C(20)	1.356(12)
Cu(1)···Cu(2)	3.040(2)		
O(1)–Cu(1)–O(1 ⁱ)	155.8(5)	O(1)–Cu(2)–O(2)	78.1(3)
O(1)–Cu(1)–O(2 ⁱ)	100.1(3)	O(1)–Cu(2)–C(9)	95.3(3)
O(1 ⁱ)–Cu(1)–O(2 ⁱ)	85.2(3)	O(2)–Cu(2)–C(9)	94.4(3)
O(2)–Cu(1)–O(2 ⁱ)	154.5(6)	O(1)–Cu(2)–C(10)	112.5(3)
O(1)–Cu(2)–C(19)	93.4(3)	O(2)–Cu(2)–C(10)	129.5(3)
O(2)–Cu(2)–C(19)	95.4(3)	O(1)–Cu(2)–C(20)	128.4(3)
C(9)–Cu(2)–C(19)	168.1(3)	O(2)–Cu(2)–C(20)	111.3(3)
C(10)–Cu(2)–C(19)	130.8(3)	C(9)–Cu(2)–C(20)	132.1(3)
C(10)–Cu(2)–C(20)	99.7(3)		

respect to copper(II). Coordination to a single copper(I) centre by two alkene groups from different ligands appears to be rare and, to our knowledge, only three previous examples have been reported.⁷

Presumably, partial oxidation resulting from oxygen seepage yields a complex retaining four 2-allyl-6-methylphenoxide ligands but with only three metal centres, one of which, Cu(I), is divalent. Disproportionation cannot, of course, be ruled out, but we have no evidence for the formation of metallic copper. Unfortunately, since we have not been able to repeat the reaction, despite many attempts using controlled addition of oxygen, we can but speculate as to the nature of the process leading to the formation of the mixed-valence species. One possibility might be oxidation with the concomitant formation of colloidal copper(I) oxide, which could contribute to the dark-red colour of the mother liquor:



where $\text{L} = ^-\text{OC}_6\text{H}_3(\text{CH}_3)[\text{CH}_2\text{C}(\text{H})=\text{CH}_2]$. On the other hand, cuprous oxide is insoluble in toluene and we have no evidence for the formation of a precipitate. It therefore seems more likely that oxidation would result in the formation of soluble organocopper(I)oxide containing species, such as $[\text{Cu}_{10}\text{O}_2(\text{Mes})_6]$ (which is orange-red),⁸ as by-products. Controlled addition of oxygen proved successful in reproduction and elucidation of the reaction between oxygen and mesitylcopper, which resulted in the formation of an oxidomesitylcopper(I) intermediate, $[\text{Cu}_{10}\text{O}_2(\text{Mes})_6]$, following dioxygen cleavage accompanied by oxidatively induced reductive elimination of bimesityl.⁸ On addition of oxygen to the crystals and mother liquor of 2-allyl-6-methylphenoxocopper(I) at -80°C , the solution undergoes a colour change to red but, as yet, without formation of crystals of $[\text{Cu}_3\{\text{OC}_6\text{H}_3-$

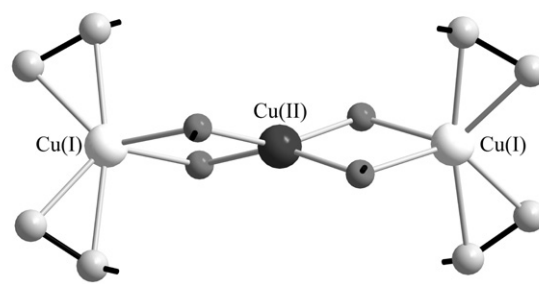


Fig. 2 A schematic view of **1** showing the distorted square-planar copper(II) centre and the tetrahedrally coordinated copper(I) centres. Parts of the 2-allyl-6-methylphenoxide ligands have been omitted for clarity.

$(\text{CH}_3)[\text{CH}_2\text{C}(\text{H})=\text{CH}_2]\}_4] \cdot 2\text{C}_6\text{H}_5(\text{CH}_3)$ (**1**). Attempts to elucidate the mechanism for the formation of **1** are continuing.

Albeit by an uncertain route, partial oxidation or disproportionation of tetrameric 2-allyl-6-methylphenoxocopper(I) affords a trinuclear mixed-valence alkoxide in which copper(II) is bonded solely to the hard oxygen donor whereas the copper(I) centre co-ordinates two soft alkene linkages and two oxygen donors. As is seen from Fig. 2 and Table 1, the co-ordination geometry of the central copper atom is that of a distorted square-planar copper(II) centre, whereas the peripheral copper centres exhibit a distorted tetrahedral environment, typical of copper(I). The complex is therefore best characterised as a Robin and Day⁹ class I mixed-valence species, although the dark-red colour indicates some transfer of charge between the centres, which would suggest borderline class II behaviour. In recently prepared bromocuprate(I,II) species,^{10a,b} the copper centres are equivalent or nearly equivalent such that these compounds exhibit typical class III and class II behaviour, respectively, with intermediate formal charges between one and two on the metal centres.¹⁰

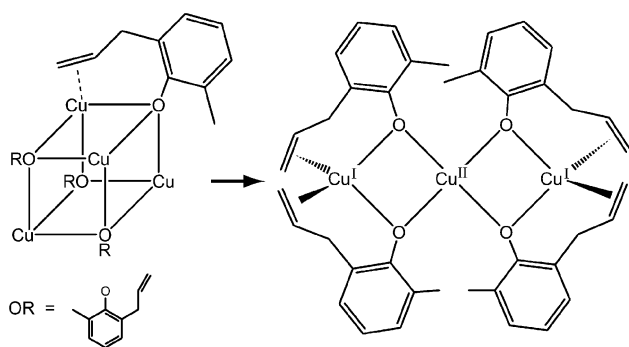
In **1**, the Cu(I)···Cu(II) distance is 3.040(2) Å, which is of the order of that in a mixed-valence Cu(I)/Cu(II) chlorocuprate reported by Willett.¹¹ Here the interactions between the copper centres were demonstrated by Sherwood and Hoffmann¹² to arise principally through the bridging ligands. In an early example of an oxygen-bridged mixed-valence copper(I)/copper(II) complex with clearly distinguishable metal centres,¹³ the Cu(I)···Cu(II) separation is also rather large, *viz.* 3.269(1) Å. Typical class III behaviour would seem to more often result in shorter Cu···Cu distances of the order of 2.4 Å.^{10a,14} In the case of the $[\text{Cu}_2\text{Br}_3]^{2-}$ ion, however, the very short distance of 2.36 Å has been demonstrated to be associated with an energetically weak and soft Cu···Cu interaction.^{10a}

Experimental

Synthesis of compound 1

All operations were performed under nitrogen or argon atmosphere using standard Schlenk techniques at ambient temperature or special low-temperature methodology.¹⁵ Solvents were freshly distilled from sodium/benzophenone. Mesitylcopper(I) was prepared from copper(I) chloride,¹⁶ 2-bromomesitylene and magnesium according to procedures described in the literature.^{5c,17}

Mesitylcopper (0.35 mmol; 0.065 g) was dissolved in toluene (9 ml) and an excess of 2-allyl-6-methylphenol (0.88 mmol; 0.13 ml) was added slowly with a syringe. The resulting solution was stirred for a few seconds, during which time it changed colour from yellow to orange. After storage of the solution at -80°C for 4 days an orange precipitate and pale-yellow rod-shaped crystals of $[\text{Cu}_4\{\text{OC}_6\text{H}_3(\text{CH}_3)[\text{CH}_2\text{C}(\text{H})=\text{CH}_2]\}_4]$ ^{4e} were deposited. Continued storage at -80°C for several weeks



Scheme 1

afforded red cubes of $[\text{Cu}_3\{\text{OC}_6\text{H}_3(\text{CH}_3)[\text{CH}_2\text{C}(\text{H})=\text{CH}_2]\}_4] \cdot 2\text{C}_6\text{H}_5(\text{CH}_3)$ (**1**) in approximately 10% yield from a dark red solution. Although it seems likely that the formation of a mixed-valence alkoxide can be attributed to oxygen seepage, it has not yet been possible to repeat the reaction by controlled addition of oxygen.

X-Ray crystallography

A crystal of **1** was mounted under argon in a glass capillary at -155°C^{15} and transferred in liquid nitrogen to a Rigaku AFC6R diffractometer. Diffracted intensities were measured using graphite-monochromated Mo $\text{K}\alpha$ ($\lambda = 0.710\ 73\ \text{\AA}$) radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). Data were recorded at -141°C for $4 < 2\theta < 50^\circ$ from a red cubic-shaped crystal with approximate dimensions $0.15 \times 0.15 \times 0.15\ \text{mm}$, using the ω - 2θ scan mode with an ω scan rate of $8^\circ\ \text{min}^{-1}$ and a scan width of $(0.71 + 0.30 \tan\theta)^\circ$. 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 four 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 in the range $12.3 < 2\theta < 17.0^\circ$. Correction was made for Lorentz and polarisation effects. No correction was made for the effects of absorption. The structure was solved by direct methods (SIR 92)¹⁸ and refined using full-matrix least-squares calculations on F^2 (SHELXL-97)¹⁹ operating in the WinGX programme package.²⁰ Anisotropic thermal displacement parameters were refined for all the non-hydrogen atoms and the hydrogen atoms were included using the riding model. Refinement of 255 parameters based on all 4083 reflections yielded $R_1 = 0.064$ and $wR_2 = 0.147$ for the 1072 reflections for which $I > 2\ \sigma(I)$, and $wR_2 = 0.231$ for all reflections; maximum and minimum residual electron density was 0.75 and $-1.06\ \text{e}\ \text{\AA}^{-3}$. Structural illustrations (Figs. 1 and 2) have been drawn with ORTEP-3 for Windows²¹ and Diamond,²² respectively.

$[\text{Cu}_3\{\text{OC}_6\text{H}_3(\text{CH}_3)[\text{CH}_2\text{C}(\text{H})=\text{CH}_2]\}_4] \cdot 2\text{C}_6\text{H}_5(\text{CH}_3)$ (**1**): $\text{C}_{54}\text{H}_{60}\text{Cu}_3\text{O}_4$, $M_r = 963.6$, monoclinic, space group $C2/c$, $a = 23.930(6)$, $b = 8.041(3)$, $c = 25.014(5)\ \text{\AA}$, $\beta = 105.74(2)^\circ$, $U = 4633(2)\ \text{\AA}^3$, $Z = 4$, $\mu = 1.410\ \text{mm}^{-1}$.

CCDC reference number 195553. See: <http://www.rsc.org/suppdata/nj/b2/b211899h> for crystallographic data in CIF format or other electronic format.

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