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A tetranuclear copper compound containing three different types of anions: *trans*-(*μ*-*tert*-butoxy)bis(*μ*-2,4,6,2″,4″,6″-hexamethyl-1,1′:3′,1″-terphenyl-2′,2′-diyl)(*μ*-iodo)tetracopper(I)

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The title compound $[(CuDmp)_2(CuI)(CuO^tBu)]$ (Dmp = 2,6-$Mes_2C_6H_3$ with Mes = 2,4,6–$Me_3C_6H_2$), $[Cu_4I(C_4H_9O)(C_{24}H_{25})_2]$, was obtained as by-product of the synthesis of the copper aryl $(CuDmp)_2$. It contains an almost planar central Cu_4C_2IO ring with two-coordinate Cu atoms and two different sets of Cu—C distances (average Cu—C = 1.952 and 2.032 Å; average Cu—O = 1.859 Å; average Cu—I = 2.4478 Å).

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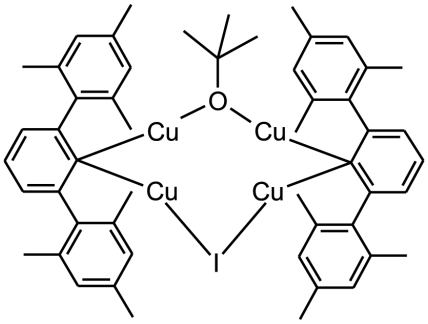
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.007 Å
R factor = 0.035
wR factor = 0.059
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The preparation of organocopper compounds of the type RCu usually involves the reaction of a copper(I) halide with an organolithium or -magnesium reagent in donor solvents like Et_2O, THF or DMS (van Koten *et al.*, 1995). A commonly encountered problem of this method is the contamination of the desired copper compounds with lithium or magnesium halides and the formation of stable mixed organocopper copper halide aggregates (Janssen *et al.*, 1996, and references cited therein). The use of copper *tert*-butoxide as an alternative halide-free starting material has recently permitted the preparation of the copper aryls $CuC_6H_3Ph_2$-2,6 and $CuC_6H_3Mes_2$-2,6 which are trimeric and dimeric, respectively, in the solid state (Niemeyer, 1998). As by-product of the synthesis of the latter compound the title complex, (I), has now been isolated in small yield.



(I)

The molecular structure of (I) shows a tetranuclear copper aggregate (Fig. 1) which consists of two *trans*-arylcopper moieties and one copper iodide and copper *tert*-butoxide unit, respectively. The almost planar central Cu_4C_2IO ring (Fig. 2) [the largest deviations from planarity are 0.075 (2) Å for Cu4 and 0.059 (3) Å for C25] features two-coordinate Cu atoms with an approximately linear environment [O—Cu1—C1

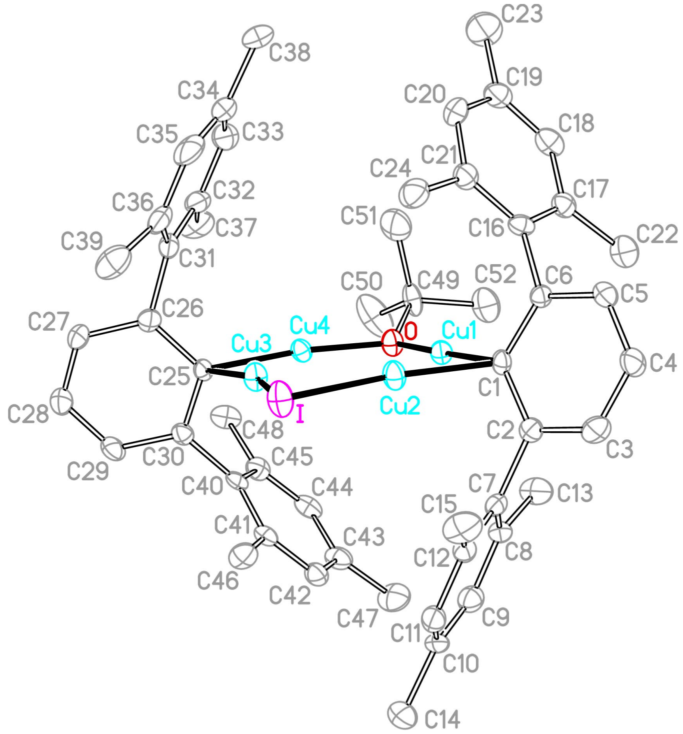


Figure 1
Displacement ellipsoid plot (at the 35% probability level) of (I). H atoms have been omitted for clarity.

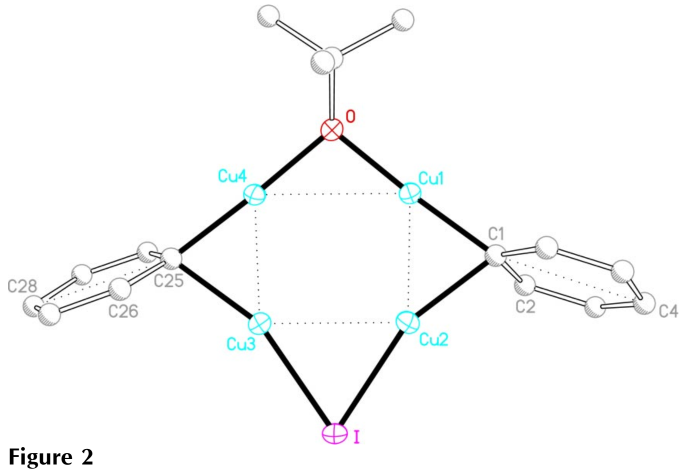


Figure 2
View perpendicular to the central Cu_4C_2IO ring. Mes substituents and H atoms have been omitted for clarity.

176.84 (14), C1—Cu2—I 160.42 (11), C25—Cu3—I 160.20 (11) and O—Cu4—C25 172.67 (16)°]. There are two different sets of Cu—C bond lengths. Shorter Cu1—C1 and Cu4—C25 distances [1.946 (4) and 1.957 (4) Å] and larger Cu1—C1···C4 and Cu4—C25···C28 angles [161.7 (2) and 161.2 (2)°] alternate with larger and smaller values for Cu2—C1 and Cu3—C25 [2.031 (4) and 2.033 (4) Å], and Cu2—C1···C4 and Cu3—C25···C28 [124.8 (2) and 125.1 (2)°], respectively. Therefore, the bonding to the aryl C_{ipso} atoms can be described as an alternating 2*e*-2*c* C_{ipso}—Cu and π-type C_{ipso}—Cu interaction. This view is in agreement with the alternative formulation of (I) as a contact ion pair $[Cu_2I]^+[Cu_2(Dmp)_2(O^tBu)]^-$. Similar A-frame-shaped anions were recently found in the compounds $[Li(thf)_4][Dmp(CuI)_2]$ (Hwang & Power, 1999) and $[Li_7(O^tBu)_6][Cu_2\{Si(SiMe_3)_3\}_2]$ (Klinkhammer, 2000). In contrast to the Cu—C bonding, a rather symmetric bridging interaction is observed to the iodo [Cu2—I 2.4457 (6) Å and Cu3—I 2.4499 (6) Å] and *tert*-butoxide [Cu1—O 1.856 (3) Å and Cu4—O 1.861 (3) Å] ligands. With values of 2.3761 (7) (Cu1···Cu2), 2.3765 (7) (Cu3···Cu4), 2.7226 (8) (Cu2···Cu3) and 2.8578 (8) Å (Cu1···Cu4), the non-bonding copper–copper separations are of the same magnitude as previously observed for other copper organyls. A unique feature in (I) is the presence of a Cu—I—Cu bridge in which all three atoms possess coordination number 2.

Experimental

A solution of ^{n}BuLi (3.00 mmol) in 1.2 ml of hexane was added at ambient temperature to DmpI (1.07 g, 3.00 mmol) in 20 ml of toluene. After 2 h, CuO^tBu (0.41 g, 3.00 mmol) was added *via* a solid-addition tube and stirring was continued for 14 h. The resulting amber solution was concentrated under reduced pressure. Cooling in a 248 K freezer afforded colorless crystals of $(CuDmp)_2$ in 55% yield. All volatile materials were removed from the mother liquor and the residue was redissolved in a small amount of diethyl ether. After cooling to 248 K, colorless needles of (I) were obtained in *ca* 3% yield. The origin of the CuI content in (I) can be explained by the presence of LiI impurities (formed by a side reaction from ^{n}BuLi and ^{n}BuI) followed by an exchange reaction with CuO^tBu. M.*p*.: crystals change color to orange > 353 K and decompose to a black liquid at 497–501 K. IR (Nujol, cm^{-1}): 1610 (*m*), 1358 (*m*), 1173 (*m*), 1080 (*w*), 1028 (*m*), 1014 (*w*), 942 (*m*), 845 (*s*), 801 (*ms*), 770 (*w*), 740 (*s*), 716 (*ms*), 625 (*m*), 589 (*w*), 570 (*m*), 545 (*w*), 506 (*w*), 385 (*w*). EI–MS (70 eV): *m*/*z* (%) 1078.3 (0.003%) [M^+ with ^{63}Cu].

Crystal data

$[Cu_4I(C_{24}H_{25})_2(C_4H_9O)]$
$M_r = 1081.05$
Triclinic, $P\bar{1}$
$a = 12.3307\ (14)$ Å
$b = 12.6105\ (10)$ Å
$c = 16.3613\ (12)$ Å
$\alpha = 89.734\ (6)°$
$\beta = 80.137\ (7)°$
$\gamma = 72.592\ (9)°$
$V = 2388.8\ (4)$ Å^3

$Z = 2$
$D_x = 1.503$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
$\theta = 11.5$–$12.5°$
$\mu = 2.44$ mm^{-1}
$T = 173\ (2)$ K
Needle, colorless
0.70 × 0.15 × 0.05 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.280$, $T_{max} = 0.888$
9829 measured reflections
9372 independent reflections
5430 reflections with $I > 2\sigma(I)$

$R_{int} = 0.050$
$\theta_{max} = 26.0°$
$h = -15 \rightarrow 15$
$k = -14 \rightarrow 15$
$l = -19 \rightarrow 20$
2 standard reflections every 198 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.059$
$S = 0.72$
9372 reflections
594 parameters

Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0129P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—C1	1.946 (4)	Cu4—O	1.861 (3)
Cu1—O	1.856 (3)	Cu4—C25	1.957 (4)
Cu2—C1	2.031 (4)	Cu1—Cu2	2.3761 (7)
Cu2—I	2.4457 (6)	Cu1—Cu4	2.8578 (8)
Cu3—C25	2.033 (4)	Cu2—Cu3	2.7227 (8)
Cu3—I	2.4499 (6)	Cu3—Cu4	2.3766 (7)
O—Cu1—C1	176.84 (14)	Cu2—I—Cu3	67.58 (2)
C1—Cu2—I	160.42 (11)	Cu1—O—Cu4	100.51 (13)
C25—Cu3—I	160.20 (11)	Cu1—C1—Cu2	73.33 (14)
O—Cu4—C25	172.67 (16)	Cu4—C25—Cu3	73.07 (13)

The H atoms were placed in idealized positions and refined in a riding-model approximation, including free rotation for methyl groups. For most H atoms the assigned $U_{\rm eq}$ was allowed to refine freely. Isotropic displacement parameters larger than 0.15 were constrained to 1.2 $U_{\rm eq}$ of the parent atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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