A Stable Trinuclear Mixed (Organic)(organo)copper Cluster: Synthesis and Structure of Bis(benzoato)(mesityl)tricopper(I)

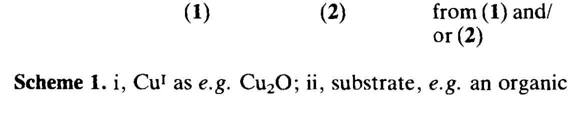
Henk L. Aalten,[a] Gerard van Koten,*[a] Kees Goubitz,[b] and Casper H. Stam[b]

[a] *Anorganisch Chemisch Laboratorium and* [b] *Laboratorium voor Kristallografie, J. H. van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

The interaggregate exchange reaction of Cu_5Mes_5 (Mes = $C_6H_2Me_3$-2,4,6) with $Cu_4(OBz)_4$ (OBz = O_2CPh) in benzene or toluene afforded the trinuclear cluster $Cu_3Mes(OBz)_2$ (40% yield) with two bridging benzoato groups [Cu–O 1.862 Å (mean); bridged Cu $\cdots$ Cu 2.888(2) Å] and one bridging, three-centre, two-electron bonded mesityl group [Cu–C 1.957(6) Å; bridged Cu $\cdots$ Cu 2.421(2) Å].

The copper induced decarboxylation of aromatic carboxylic acids, which has been explored in organic synthesis for bringing about new C–O and C–C bonds, is generally believed to proceed *via* copper(I) carboxylates (**1**) and arylcopper(I) compounds (**2**)[1] as intermediates (see Scheme 1). Even pure organocopper compounds (*i.e.*, pentafluorophenylcopper[2] and cyanomethylcopper[3]) have been isolated *via* decarboxylation of copper(I) carboxylates.

Somewhat more recently the insertion reaction of carbon dioxide with transition metal complexes has become of interest because carbon dioxide represents a source of non-fossil carbon which is not extensively exploited in catalytic reactions or processes.[4]



$$\mathrm{RCO_2H} \xrightarrow{\text{i}} [\underset{(\mathbf{1})}{\mathrm{RCO_2Cu}} \underset{\mathrm{CO_2}}{\overset{-\mathrm{CO_2}}{\rightleftarrows}} \underset{(\mathbf{2})}{\mathrm{RCu}}] \xrightarrow{\text{ii}} \text{C–O and/or C–C coupling products originating from (1) and/or (2)}$$

Scheme 1. i, Cu^I as *e.g.* Cu_2O; ii, substrate, *e.g.* an organic halide.

We report here the synthesis and structure of a trinuclear copper(I) cluster which not only is the first example of a mixed (organic)(organo)copper cluster but also may serve as a model for the intermediates formed during CO_2 insertion (or elimination) reactions involving Cu–C bonds.

The title compound, $Cu_3Mes(OBz)_2$ (Mes = $C_6H_2Me_3$-2,4,6; OBz = O_2CPh), (**3**), was formed by an interaggregate exchange between mesitylcopper(I) pentamer[5] (3 mmol)† and copper(I) benzoate tetramer[6] (3 mmol)† in benzene or toluene (50 ml) and isolated by adding hexane to the filtered reaction mixture (yield 40%).‡ Crystals suitable for an *X*-ray structure determination were obtained by vapour diffusion of pentane to the filtered reaction mixture.

---

† Calculated on the monomeric unit.

‡ Satisfactory elemental analyses were obtained (C, H, Cu, O). *N.m.r. data:* δ_H (100 MHz; solvent C_6D_6; standard Me_4Si) 2.07 (3H, s, *p*-Me), 2.67 (6H, s, *o*-Me), 6.7—7.2 (8H, m, *m*-, *p*-Ar), and 8.05 (4H, br, *o*-Ar). The 2:1 ratio of OBz and Mes groups was further established by reacting (**3**) with DCl/D_2O and determining the $PhCO_2D$: 2,4,6-$Me_3C_6H_2D$ ratio by n.m.r. spectrometry.

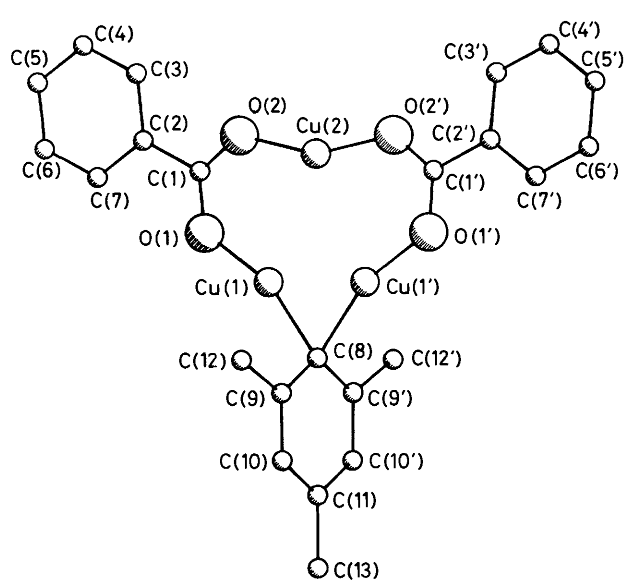


Figure 1. Pluto drawing of trinuclear (**3**). Selected bond distances (Å) and angles (°): Cu(1)–O(1) 1.868(5), Cu(1)–C(8) 1.957(6), Cu(1) ··· Cu(1') 2.421(2), Cu(1) ··· Cu(2) 2.888(2), Cu(2)–O(2) 1.855(5), O(1)–C(1) 1.265(8), O(2)–C(1) 1.232(8), C(8)–C(9) 1.427(6); C(8)–Cu(1)–O(1) 161.2(2), O(2)–Cu(2)–O(2') 156.6(2), Cu(1)–Cu(2)–Cu(1') 49.55(05), Cu(1)–C(8)–Cu(1') 76.4(3), C(9)–C(8)–C(9') 118.0(6), Cu(1)–O(1)–C(1) 123.9(4), O(1)–C(1)–O(2) 125.1(6), C(1)–O(2)–Cu(2) 131.4(4).

Crystal data: crystals of the title compound are monoclinic, space group $C2/c$, with 4 formula units $C_{23}H_{21}O_4Cu_3$ in a unit cell of dimensions $a = 16.926(2)$, $b = 11.781(1)$, $c = 10.763(1)$ Å and $\beta = 94.48(1)°$, $U = 2139.6(6)$ Å^3, $D_c = 1.71$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 36.3$ cm^{-1}. The structure was solved by SIMPEL[7] and refined anisotropically only for the copper atoms by full-matrix least-squares. An empirical absorption correction was applied.[8] The current R is 0.059 for 1627 reflections collected at room temperature on a NONIUS CAD4 diffractometer in the range $\theta < 70°$.§

$Cu_3Mes(OBz)_2$

(**3**)

Figure 1 shows the unique trinuclear structure of (**3**) and some relevant bond distances and angles. The two benzoato fragments are each bonded as a four-electron donor to a pair of Cu atoms while the mesityl group is three-centre, two-electron bonded to two copper atoms.

The Cu(1)–O(1) and the Cu(2)–O(2) distances [1.868(5) and 1.855(5) Å, respectively] are in the range expected for bridging carboxylates.[6,9] The Cu(1)–C(8) distance is 1.957(6) and is comparable to those found recently by Floriani *et al.* in pure Cu_5Mes_5.[5] An interesting structural feature of (**3**) is the almost planar arrangement of the central ten-membered ring comprising the copper as well as the bridging carbon and oxygen atoms (puckering factor $Q^{10} = 0.26$). This planarity contrasts with the out of the Cu_4 plane co-ordination of the OBz group in Cu_4OBz_4.[6] The Cu ··· Cu distances of 2.888(2) and 2.421(2) Å reflect the specific bridging bonding modes of the carboxylato and aryl groups (the range for Cu ··· Cu distances bridged by three-centre, two-electron bonds is 2.37[11]—2.53[12] Å).

It must be noted that (**3**) is the most thermally stable compound of a series of derivatives with $Cu_3R^1(O_2CR^2)_2$ stoicheiometry. We have observed that the stability of these trinuclear copper compounds can be affected in two ways (i) by the presence of *ortho* substituents in the bridging aryl group (R^1) and (ii) by the presence of an *ortho* Cl substituent in R^2. The first factor, which stabilizes these trinuclear copper compounds, can be attributed to the stabilization of the perpendicular position of R^1 with respect to the Cu ··· Cu vector [87.5° in (**3**)] thus stabilizing the Cu_2C bond (see ref. 12 for a discussion). The destabilizing influence of the second factor is not yet understood.

The isolation of (**3**) and related mixed (organic)(organo) copper species indicates that during the copper mediated decarboxylation reactions interaggregate reactions between species (**1**) and (**2**) (see Scheme 1) may occur. The properties of these novel mixed copper species in C–O and C–C coupling reactions is currently being investigated by the study of the reactivity of (**3**) and other mixed (organic)(organo)copper clusters towards CO_2 and electrophiles as well as the influence of co-ordinating solvents on these reactions.

These investigations were supported by the Netherlands Technology Foundation (S.T.W.). OCE-Andeno B.V. (Venlo) is thanked for stimulating this project.

Received, 9th May 1985; Com. 625

References

1 T. Cohen, R. W. Berninger, and J. T. Wood, *J. Org. Chem.*, 1978, **43**, 837 and references therein.

2 A. Cairncross, J. R. Roland, R. M. Henderson, and W. A. Sheppard, *J. Am. Chem. Soc.*, 1970, **92**, 3187.

3 T. Tsuda, T. Nakatsuka, T. Hirayama, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 1974, 557.

4 D. J. Darensbourg and R. A. Kudaroski, in 'Advances in Organometallic Chemistry,' eds. F. G. A. Stone and R. West, Academic Press, London, 1983, vol. 22, pp. 129—168.

5 T. Tsuda, T. Yazawa, K. Watanabe, T. Fujii, and T. Saegusa, *J. Org. Chem.*, 1981, **46**, 192; S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1156.

6 M. G. B. Drew, D. A. Edwards, and R. Richards, *J. Chem. Soc., Dalton Trans.*, 1977, 299.

7 A. R. Overbeek and H. Schenk, 'Computing in Crystallography,' Delft University Press, Delft, 1978.

8 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

9 M. G. B. Drew, D. A. Edwards, and R. Richards, *J. Chem. Soc., Chem. Commun.*, 1973, 124; R. D. Mounts, T. Ogura, and Q. Fernando, *Inorg. Chem.*, 1974, **13**, 802; P. F. Rodesiler and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1974, 599.

10 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.

11 G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, 1975, **84**, 129.

12 R. W. M. ten Hoedt, J. G. Noltes, G. van Koten, and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1978, 1800.

---

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.