

Contribution from the Anorganisch Chemisch Laboratorium and the Laboratorium voor Kristallografie, J. H. van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

## The Hurtley Reaction. 2. Novel Complexes of Disubstituted Acetylenes with Copper(I) Benzoates Having a Reactive Ortho C-Cl or C-Br Bond. X-ray Structural Characterization of Tetrakis(2-chlorobenzoato)bis(diethyl acetylenedicarboxylate)tetracopper(I)

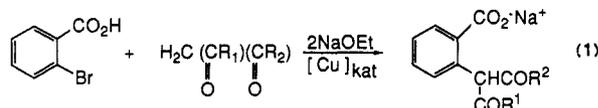
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Tetrameric copper(I) benzoate,  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$  (**1a**), and the *o*-halogen-substituted copper(I) benzoates  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})]_4$  (**1b**) and  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Br})]_4$  (**1c**), the postulated intermediates in the Hurtley reaction, react with the activated disubstituted acetylenes dimethyl acetylenedicarboxylate (DMAD) and diethyl acetylenedicarboxylate (DEAD) in diethyl ether to yield the stable, soluble, tetranuclear complexes  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})_4(\mu\text{-DMAD})_2]$  (X = H (**2a**), Cl (**2b**), Br (**2c**)) and  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})_4(\mu\text{-DEAD})_2]$  (X = H (**3a**), Cl (**3b**), Br (**3c**)). The reaction of **1b** and **1c** with diphenylacetylene in diethyl ether yields the dinuclear complexes  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})(\text{PhC}\equiv\text{CPh})]_2$  (X = Cl (**4b**), Br (**4c**)). In methanol the reaction of  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$  (**1a**) with DMAD shows a different reactivity pattern, leading to the trimerization of the alkyne. An X-ray structure determination of **3b** ( $\text{C}_{44}\text{H}_{36}\text{Cl}_4\text{Cu}_4\text{O}_{16}$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.973$  (3) Å,  $b = 20.926$  (4) Å,  $c = 10.949$  (4) Å,  $\alpha = 96.76$  (2)°,  $\beta = 90.96$  (3)°,  $\gamma = 104.55$  (3)°, and  $Z = 2$ ) has been carried out. The structure, refined to a final *R* factor of 0.053 with use of 7016 reflections, shows it to be the first copper(I) benzoate compound wherein four copper(I) atoms form a distorted-tetrahedral core. Each of the four benzoate units, acting as a four-electron donor, bridges two adjacent copper atoms ( $\text{Cu}\cdots\text{Cu} = 3.027$  Å (av)). The two remaining edges of the tetrahedral copper(I) core ( $\text{Cu}\cdots\text{Cu} = 2.950$  Å (av)) are each perpendicularly bridged by an acetylene unit acting as a four-electron donor; this is the first example of this bonding mode of unsaturated organic compounds in Cu(I) benzoates. All copper atoms have an almost trigonal surrounding consisting of two oxygen atoms (of different benzoates) and the midpoint of the acetylene triple bond. Our attempts to elucidate the structure of the analogous bromo compound **2c** were only partially successful due to strong pseudosymmetry in the crystals. The overall structure of **2c** appeared to be similar to that of **2b**: complex **2c**,  $\text{C}_{40}\text{H}_{28}\text{Br}_4\text{Cu}_4\text{O}_{16}$ , space group  $Pa$ ,  $P2_1/a$ , or  $P2_1/a$  (monoclinic) with  $a = 24.658$  (4) Å,  $b = 16.838$  (3) Å,  $c = 12.353$  (3) Å,  $\beta = 90.08$  (3)°, and  $Z = 4$ . Variable-temperature <sup>1</sup>H NMR spectroscopy and molecular weight determinations of complexes **2** indicate partial dissociation of the coordinated acetylene ligands in solution.

### Introduction

Recently we started a study of the mechanism of the Hurtley reaction that is schematically shown in eq 1.<sup>2,3</sup> This reaction is



synthetically important and in its most common form involves the condensation of 2-halobenzoic acids with  $\beta$ -dicarbonyls in the presence of a base (e.g., NaOH or NaH) and a copper catalyst (Cu(0), Cu(I), or Cu(II)) in solvents such as water, alcohols, or the  $\beta$ -dicarbonyl itself.

The mechanisms that have been proposed for the Hurtley reaction<sup>4</sup> all have the following characteristic features: (i) a copper(I) carboxylate unit situated ortho to the reactive C-X (X = halogen) bond is a key intermediate; (ii) the polarization of the C-X bond is augmented through coordination of the *o*-halogen atom to the copper(I) atom (see Figure 1).

Recently we succeeded in synthesizing and isolating examples of the postulated 2-halo-substituted copper(I) benzoate intermediates, i.e.  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})]_4$  (**1b**) and  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Br})]_4$  (**1c**). The structures of **1b** and **1c** could, however, not be solved unambiguously due to the insolubility of **1b** and **1c** in the few organic solvents with which they did not react. Since it is known that disubstituted acetylenes react with copper(I) benzoate,  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$  (**1a**), to yield stable dinuclear copper(I) acetylene complexes,<sup>5</sup> the same reaction of our 2-halo-substituted copper(I) benzoates has been investigated with a view to forming soluble species that would enable the study of the postulated halogen-copper interaction.

The present report concerns the reactions of  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})]_4$  (**1b**) and  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Br})]_4$  (**1c**) and copper(I) benzoate,  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$  (**1a**), with disubstituted acetylenes in both diethyl ether and methanol as solvents. The solution and solid-state characterization of the unusual products

formed is presented and the relevance of these species to the Hurtley reaction discussed.

### Experimental Section

**Reagents and General Procedures.** All reactions were carried out under dry oxygen-free nitrogen with the use of standard Schlenk techniques. Solvents were carefully dried and distilled prior to use.  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$  (**1a**)<sup>6</sup> and  $[\text{Cu}(\text{Mes})]_3$ <sup>7</sup> were synthesized according to literature procedures. Other starting materials are commercially available (Janssen Chimica).

<sup>1</sup>H NMR spectra were obtained on Bruker AC 100 or Bruker WM 250 NMR spectrometers (see Table I). <sup>13</sup>C NMR spectra were obtained on Bruker WP 80, Bruker WM 100, or Bruker WM 250 NMR spectrometers. Chemical shifts are reported in ppm downfield from Me<sub>4</sub>Si. IR spectra (Nujol) were recorded with a Perkin-Elmer 283 spectrophotometer. Cryoscopic molecular weight determinations were carried out in benzene under dry, oxygen-free nitrogen. The field ionization (FI) mass spectrum of hexamethyl mellinate was obtained with a Varian MAT711 double-focusing mass spectrometer with a combined EI/FI/FD source. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

**Preparative Procedures.** Syntheses of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})_4(\mu\text{-DMAD})_2]$  (X = H (**2a**), Cl (**2b**), Br (**2c**)) and  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})_4(\mu\text{-DEAD})_2]$  (X = H (**3a**), Cl (**3b**), Br (**3c**)). Dialkyl acetylenedicarboxylate (2.44 mmol) was added to an ethereal suspension (30 mL)

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Table I.  $^1\text{H}$  NMR Data for  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})_4(\text{RC}\equiv\text{CR})_2]^{a,b}$ 

compd	solvent	temp, K	benzoato ligand				RC $\equiv$ CR ligand	
			H2, H6	H3	H4	H5	CH <sub>3</sub>	CH <sub>2</sub>
DMAD	benzene- <i>d</i> <sub>6</sub>	298					3.15 s	
		373					3.52 s	
	tol- <i>d</i> <sub>8</sub>	293					3.40 s	
		233					3.26 s	
$[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\text{DMAD})_2]$	benzene- <i>d</i> <sub>6</sub>	298	8.27 br		7.16 br, m		2.86 s	
		298	8.41 br		7.20–7.33 m		3.19 br	
	tol- <i>d</i> <sub>8</sub>	293	8.47 br		7.21–7.33 m		3.13 br, s	
		253	8.50 dd, br		7.22–7.38 m		3.05 s	
	233	8.52 dd, br		7.22–7.37 m		3.01 s		
		213	8.55 dd, br		7.19–7.42 m		2.95 s	
$[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\text{DMAD})_2]$	tol- <i>d</i> <sub>8</sub> <sup>c</sup>	293	8.03 br	<i>d</i>	7.02 br, m		3.39 br, s	
		253	7.89 m	<i>d</i>	7.00 m		3.31 s	
	233	7.76 br	<i>d</i>	7.00 m		3.26 s		
		213	7.56 br	<i>d</i>	7.00 m		3.22 s	
$[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Br})_4(\text{DMAD})_2]$	benzene- <i>d</i> <sub>6</sub>	298	7.76 dd	7.34 d	6.57–6.88 m		3.12 s	
		293	8.04 dd, br	7.55 m	7.09 m	6.92 m	3.40 br, s	
	253	7.82 br	7.53 m	7.06 m	6.92 m	3.33 s		
		233	7.65 br	7.48 m	7.04 m	6.90 m	3.28 s	
	213	7.51 m	7.03 m	6.90 m		3.23 s		
DEAD	tol- <i>d</i> <sub>8</sub>	293					1.08 t	3.95 q
		233					0.98 t	3.88 q
$[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\text{DEAD})_2]$	tol- <i>d</i> <sub>8</sub> <sup>c</sup>	253	8.45 dd		7.29–7.48 m		0.67 t	3.72 q
$[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\text{DEAD})_2]$	tol- <i>d</i> <sub>8</sub> <sup>c</sup>	253	8.10 dd	7.28 dd	7.00 m		0.81 t	3.89 q
$[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Br})_4(\text{DEAD})_2]$	tol- <i>d</i> <sub>8</sub> <sup>c</sup>	253	8.11 br	7.51 dd	7.04 m	6.88 m	0.78 t	3.78 q

<sup>a</sup> Recorded on a Bruker AC 100 NMR spectrometer unless stated otherwise; all values are in ppm relative to external TMS. Abbreviations: s = singlet; d = doublet; dd = doublet; t = triplet; q = quartet; m = multiplet; br = broad. <sup>b</sup>  $^1\text{H}$  NMR spectra of the diphenylacetylene complexes could not be obtained due to their low solubility. <sup>c</sup> Recorded on a Bruker WM 250 NMR spectrometer. <sup>d</sup> Obscured by solvent.

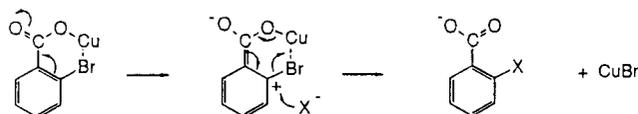


Figure 1. Proposed polarization of the ortho C-X bond by intramolecular Cu(I) coordination in the intermediates of the Hurtley reaction.

of  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})_4]$  (0.5 mmol; X = H (1a), Cl (1b), Br (1c)), and a yellow suspension was immediately formed. This reaction mixture was stirred at room temperature for 16 h, after which the yellow product was filtered off and washed with diethyl ether (3  $\times$  10 mL) and hexane (2  $\times$  10 mL); yield 70–80% of 2 or 3.

Crystals of 2c and 3b suitable for an X-ray analysis were obtained by cooling the filtrate (excluding washings) to  $-20^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{44}\text{H}_{40}\text{Cu}_4\text{O}_{16}$  (3a): C, 48.97; H, 3.73; O, 23.73. Found: C, 48.70; H, 3.86; O, 24.10. Calcd for  $\text{C}_{44}\text{H}_{36}\text{Cl}_4\text{Cu}_4\text{O}_{16}$  (3b): C, 43.43; H, 2.98; Cl, 11.65; Cu, 20.89; O, 21.04. Found: C, 43.02; H, 3.18; Cl, 11.42; Cu, 21.21; O, 20.62. Calcd for  $\text{C}_{44}\text{H}_{36}\text{Br}_4\text{Cu}_4\text{O}_{16}$  (3c): C, 37.89; H, 2.60; Br, 22.91; Cu, 18.23; O, 18.35. Found: C, 37.49; H, 2.89; Br, 23.54; Cu, 18.88; O, 18.16. IR (Nujol): 2a, 3a, 1725  $\text{cm}^{-1}$  (br, COOR); 2b, 3b, 1721  $\text{cm}^{-1}$  (br, COOR); 2c, 3c, 1722  $\text{cm}^{-1}$  (br, COOR). Molecular weight found (calcd for the tetrameric unit): 2a, 496 (1023); 2b, 520 (1160); 2c, 660 (1338).  $^1\text{H}$  NMR data are summarized in Table I.

**Attempted Synthesis of  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})(\text{PhC}\equiv\text{CPh})_2]$  (X = Cl (4b), Br (4c)).** To a suspension of  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})_4]$  (0.5 mmol; X = Cl (1b), Br (1c)) in diethyl ether (30 mL) at room temperature was added diphenylacetylene (0.446 g, 2.5 mmol). The white precipitate that was formed after 20 h was filtered off and washed subsequently with diethyl ether (3  $\times$  10 mL) and hexane (2  $\times$  10 mL). Elemental analysis revealed that the white precipitate consisted mainly (over 80%) of  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-X})(\text{PhC}\equiv\text{CPh})_2]$  (X = Cl (4b), Br (4c)) in addition to some copper(I) benzoate starting compound. Anal. Calcd for  $\text{C}_{42}\text{H}_{28}\text{Cl}_2\text{Cu}_2\text{O}_4$  (4b): C, 63.48; H, 3.55; Cl, 8.92; Cu, 15.99; O, 8.05. Calcd for  $\text{C}_{37}\text{H}_4\text{ClCuO}_2$  (1b): C, 38.37; H, 1.84; Cl, 16.17; Cu, 29.00; O, 14.60. Found: C, 59.84; H, 3.91; Cl, 8.63; Cu, 17.74; O, 8.62. Calcd for  $\text{C}_{42}\text{H}_{28}\text{Br}_2\text{Cu}_2\text{O}_4$  (4c): C, 57.09; H, 3.19; Br, 18.09; Cu, 14.39; O, 7.24. Calcd for  $\text{C}_7\text{H}_4\text{BrCuO}_2$  (1c): C, 31.91; H, 1.53; Br, 30.32; Cu, 24.98; O, 12.14. Found: C, 55.00; H, 3.25; Br, 18.51; Cu, 15.39; O, 7.44. IR (Nujol): 4b, 4c, 1980  $\text{cm}^{-1}$  (w, C $\equiv$ C).

**Synthesis of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\mu\text{-DMAD})_2]$  (2a), by Use of Excess DMAD in Methanol.** Tetrameric copper(I) benzoate (1a; 927 mg, 1.25 mmol) was added to a solution of excess dimethyl acetylenedicarboxylate (1 mL, 8.1 mmol) in methanol (30 mL). Immediately a yellow suspension was formed and the solution turned red. This reaction mixture was stirred for 2 h, after which the yellow product was filtered off and washed with diethyl ether (3  $\times$  10 mL) and hexane (2  $\times$  10 mL); yield 60% of

$[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\mu\text{-DMAD})_2]$  (2a).

**Synthesis of Hexamethyl Mellinate from Stoichiometric Copper(I) Benzoate/DMAD Reactions.** Tetrameric copper(I) benzoate (1a; 1.031 g, 5.56 mmol based on the monomeric unit) was added to a solution of less than a 1-equiv amount of dimethyl acetylenedicarboxylate (0.6 mL, 4.9 mmol, 0.88 equiv) in methanol (30 mL). Immediately a red suspension was formed. This reaction mixture was stirred for 2 h, after which the reddish precipitate was filtered off and washed with diethyl ether (3  $\times$  10 mL) and hexane (2  $\times$  10 mL). This material appeared to be the starting compound 1a (60% recovery) contaminated with copper metal. Elemental analysis gave the following proportions (calculated for pure copper(I) benzoate): C, 6.88 (7); H, 5.41 (5); Cu, 1.17 (1); O, 2.00 (2). The combined filtrate and washings were cooled to  $-30^\circ\text{C}$ , and after 39 h a salmon-colored precipitate was formed. This was isolated by filtration and washed with diethyl ether (10 mL) and hexane (2  $\times$  10 mL); yield 200 mg (29%) of hexamethyl mellinate,  $\text{C}_6(\text{CO}_2\text{Me})_6$ .  $^1\text{H}$  NMR (benzene-*d*<sub>6</sub>, 100 MHz);  $\delta$  3.87 (Me). FD MS:  $m/e$  (relative intensity) 426 ( $\text{M}^+$ ). IR (Nujol): 1730  $\text{cm}^{-1}$  (s, br, COOR).

**Reaction of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\mu\text{-DMAD})_2]$  (2a) with Methanol-*d*<sub>4</sub>.** To 20 mg of solid  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\mu\text{-DMAD})_2]$  was added 0.5 mL of methanol-*d*<sub>4</sub>. Immediately a reddish suspension was formed. A  $^1\text{H}$  NMR spectrum of this solution showed hexamethyl mellinate to be the only soluble organic product formed.

**X-ray Structure Determination and Refinement of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\mu\text{-DEAD})_2]$  (3b).** Crystal data and other numerical details of the structure determination of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\mu\text{-DEAD})_2]$  (3b) are listed in Table II. The crystal selected for study was mounted in a glass capillary sealed under nitrogen.

A nearly regular Cu tetrahedron (edges 2.94–3.00 Å) was derived from an  $E^2$ -Patterson synthesis. The rest of the structure was obtained from subsequent Fourier syntheses. After isotropic refinement an empirical absorption correction (DIFABS<sup>8</sup>) was applied. Continued anisotropic block-diagonal least-squares refinement yielded a difference Fourier in which most of the H atoms were indicated but which also showed a number of relatively high peaks that implied disorder for at least one of the rings (C23–C28) and for two of the methyl groups (C34 and C42). The ring C23–C28 appeared to be present in two conformations rotated 180° about the bond C22–C23 with respect to each other. This gave rise to two positions for Cl4. After two alternative positions with partial occupation numbers for Cl4 (A, 0.81 (1); B, 0.19), C34 (A, 0.48 (2); B, 0.52), and C42 (A, 0.57 (2); B, 0.43) were introduced, anisotropic refinement with fixed H atoms converged to  $R = 0.053$  ( $R_w = 0.103$ ). A weighting scheme  $w = 1/(1 + F_o + 0.08F_o^2)$  was used, and the anomalous scattering of Cu and Cl was taken into account. Since



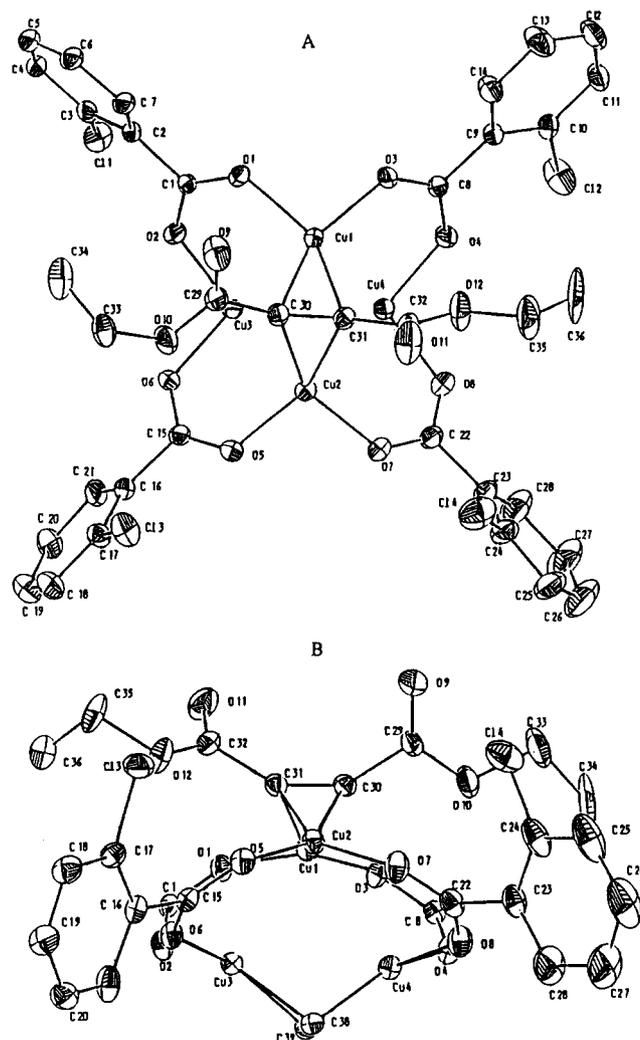
**Table IV.** Selected Interatomic Distances (Å) and Angles (deg) of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\mu\text{-DEAD})_2]$  (**3b**)

Cu...Cu			
Cu1-Cu2	2.960 (2)	Cu2-Cu3	3.001 (2)
Cu1-Cu3	2.998 (2)	Cu2-Cu4	3.129 (3)
Cu1-Cu4	2.980 (2)	Cu3-Cu4	2.941 (2)
Cu-O(carboxylate)			
Cu1-O1	1.927 (3)	Cu3-O2	1.915 (3)
Cu1-O3	1.899 (4)	Cu3-O6	1.910 (3)
Cu2-O5	1.914 (3)	Cu4-O4	1.915 (3)
Cu2-O7	1.922 (3)	Cu4-O8	1.907 (3)
Cu-C(alkyne)			
Cu1-C30	1.976 (4)	Cu3-C38	1.948 (3)
Cu1-C31	1.968 (4)	Cu3-C39	1.950 (3)
Cu2-C30	1.951 (3)	Cu4-C38	1.963 (3)
Cu2-C31	1.950 (4)	Cu4-C39	1.952 (3)
Cl-C(benzoate)			
Cl1-C3	1.742 (4)	Cl4a-C24	1.676 (6)
Cl2-C10	1.728 (4)	Cl4b-C24	1.569 (15)
Cl3-C17	1.737 (4)		
C-O(carboxylate)			
O1-C1	1.242 (4)	O5-C15	1.259 (4)
O2-C1	1.251 (4)	O6-C15	1.248 (4)
O3-C8	1.271 (5)	O7-C22	1.248 (6)
O4-C8	1.240 (4)	O8-C22	1.257 (6)
C-C(alkyne)			
C30-C31	1.280 (5)	C38-C39	1.295 (4)
In $\text{Cu}_4$ Core			
C2-Cu1-Cu3	60.48 (8)	Cu1-Cu3-Cu4	60.24 (6)
Cu2-Cu1-Cu4	63.56 (9)	Cu1-Cu4-Cu3	60.83 (8)
Cu3-Cu1-Cu4	58.93 (7)		
Around Cu1			
O1-Cu1-O3	98.3 (2)	O3-Cu1-C30	112.2 (2)
O1-Cu1-C30	142.6 (2)	O3-Cu1-C31	147.9 (2)
O1-Cu1-C31	106.5 (2)	C30-Cu1-C31	37.9 (2)
Around Cu2			
O5-Cu2-O7	96.6 (2)	O7-Cu2-C30	109.0 (2)
O5-Cu2-C30	149.8 (2)	O7-Cu2-C31	146.7 (2)
O5-Cu2-C31	113.4 (2)	C30-Cu2-C31	38.3 (2)
Around Cu3			
O2-Cu3-O6	96.2 (2)	O6-Cu3-C38	111.7 (2)
O2-Cu3-C38	146.5 (1)	O6-Cu3-C39	148.4 (2)
O2-Cu3-C39	109.1 (2)	C38-Cu3-C39	38.8 (2)
Around Cu4			
O4-Cu4-O8	96.6 (2)	O8-Cu4-C38	109.0 (2)
O4-Cu4-C38	149.5 (2)	O8-Cu4-C39	146.3 (2)
O4-Cu4-C39	112.4 (2)	C38-Cu4-C39	38.6 (2)
Around Carboxylate Atoms			
Cu1-O1-C1	127.7 (3)	Cu2-O5-C15	125.3 (3)
Cu3-O2-C1	128.5 (2)	Cu3-O6-C15	129.1 (2)
O1-C1-O2	126.4 (3)	O5-C15-O6	126.1 (3)
Cu1-O3-C8	128.7 (3)	Cu2-O7-C22	130.8 (3)
Cu4-O4-C8	127.7 (3)	Cu4-O8-C22	128.6 (3)
O3-C8-O4	125.1 (4)	O7-C22-O8	125.6 (5)
Around Alkyne C Atoms			
C29-C30-C31	147.1 (4)	C37-C38-C39	148.5 (3)
C30-C31-C32	146.4 (4)	C38-C39-C40	151.6 (3)

**2** and **3** were not found. Attempts to study the alkyne to copper(I) coordination with Raman spectroscopy were unsuccessful since **2** and **3** proved unstable under the conditions employed.

Conclusive data concerning the bonding of the alkyne ligands and the possible copper-halogen interaction in the novel 2:1 copper(I) 2-halobenzoate:alkyne complexes were obtained from a single-crystal X-ray diffraction study of **3b**.

**Solid-State Structure of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\mu\text{-DEAD})_2]$  (**3b**).** The triclinic unit cell of the crystal contains two discrete molecules. The novel tetranuclear molecular structure of this compound and the adopted numbering scheme are shown in Figure 2. Relevant bond lengths, interatomic distances, and interbond



**Figure 2.** ORTEP drawings of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\mu\text{-DEAD})_2]$  (**3b**) showing the atomic labeling (hydrogen atoms omitted, 50% thermal ellipsoids). In Figure 2A the acetylene unit bridging Cu3-Cu4 has been removed for clarity. In Figure 2B the R groups bonded to C38 and C39 and the phenyl groups bonded to C1 and C8 have been omitted for clarity.

angles are gathered in Table IV. The molecular structure of **3b** is based on a slightly distorted central copper(I) tetrahedron. Two edges of this core not sharing a common vertex (Cu1-Cu2 and Cu3-Cu4) are each bridged by an alkyne unit that is oriented perpendicularly to the copper-copper vector (Cu-C = 1.957 Å (av); C-C = 1.287 Å (av)). The four remaining edges are each bridged by the four-electron-donor carboxylate function of one of the four benzoates with a Cu-O distance of 1.914 Å (av). Accordingly, each copper atom is trigonally surrounded by two oxygen atoms of two different bridging benzoates and the midpoint of the triple bond of an acetylene unit. The copper atoms lie 0.236 Å (av) out of the plane defined by these three ligating units.

From the overall tetrahedral molecular structure of **3b** it appears as if two opposite copper atoms, of the four planar copper atoms of the starting copper(I) benzoate, have, aided by the two alkyne units, folded toward each other, yielding the distorted arrangement seen.

A prominent feature of the  $\text{Cu}_4$  core of **3b** is that the acetylene-bridged copper edges (2.950 Å av) are significantly shorter than those bridged by the benzoates. Furthermore, there is a considerable variation in the latter edge bond lengths that gives rise to the major distortion of the  $\text{Cu}_4$  cluster. This is reflected in an enlarged Cu2-Cu4 distance of 3.128 (1) Å; the average of the other benzoato-bridged copper-copper distances is 2.995 Å. This Cu2...Cu4 distance, which is the longest copper-copper distance found so far in copper(I) benzoate complexes (see Table V for a comparison of selected atomic distances and angles of

**Table V.** Selected Atomic Distances (Å) and Angles (deg) of Several Relevant Copper(I) Carboxylato and Alkyne Complexes

complex	Cu—O	Cu...Cu		Cu—C	C≡C	C≡C—R	ref
		benzoato bridged					
[Cu <sub>4</sub> (μ-O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -2-Cl) <sub>4</sub> (μ-DEAD)] <sub>2</sub>	1.899 (4)–1.927 (3)	2.941 (2)–3.129 (3)		1.948 (3)–1.976 (4)	1.288 (6) <sup>a</sup>	148.4 (7) <sup>a</sup>	b
[Cu(μ-O <sub>2</sub> CC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	1.812 (13)–1.877 (14)	2.709 (6)–2.770 (5)					10b
[Cu(μ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>4</sub> ] <sup>c</sup>	1.89	2.544					15a
[Cu(O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub> ] <sup>c</sup>	1.83–2.2	ca. 2.8		2.7–3.0			11
[Cu(μ-O <sub>2</sub> CC <sub>6</sub> H <sub>5</sub> )(PhC≡CPh) <sub>2</sub> ] <sub>2</sub>	1.933 (10)–1.987 (10)	2.779 (4) <sup>a</sup>			1.227 (av)	158.4 (av)	5
[Cu(μ-O <sub>2</sub> CC <sub>6</sub> H <sub>5</sub> )(NC <sub>9</sub> H <sub>7</sub> ) <sub>2</sub> ] <sub>2</sub>	1.944 (5)–2.107 (5)	2.638 (2)					13
[Cu <sub>2</sub> (TC-6,6)(μ-DEAD)]		2.806 (1)		1.937 (4)–1.961 (4)	1.320 (6)	137.8 (5)	18
[Cu(O <sub>2</sub> CCH <sub>3</sub> )(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> ]	2.162 (5)–2.257 (7)						14a
[Cu(O <sub>2</sub> CC <sub>6</sub> H <sub>5</sub> -2-NO <sub>2</sub> )(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> ]	2.244 (7)–2.251 (7)						14b
[Cu(NH(py)) <sub>2</sub> (C <sub>2</sub> H <sub>2</sub> )]BF <sub>4</sub>				1.971 (4)	1.188 (11)	164 (3)	17
[Cu((C <sub>6</sub> H <sub>4</sub> C≡C) <sub>3</sub> )(CF <sub>3</sub> SO <sub>3</sub> )]				2.060 (4) (av)	1.222 (10)	177.8 (6)	19

<sup>a</sup> Average of two values that do not differ significantly. <sup>b</sup> This article. <sup>c</sup> Standard deviations not given.

several copper(I) benzoate and alkyne complexes), could be an indication that the tetrameric cluster is on the way to breakdown into smaller units (vide infra).

Another very important feature of **3b** is the absence of an interaction of the 2-chloro atoms in the benzoate units with the copper atoms. All the mechanisms that have been proposed for the Hurtley reaction assume that an interaction of the copper atom with the halogen atom in a copper(I) 2-halobenzoate, as depicted in Figure 1, would account for the activation of the carbon–halogen bond. The solid-state structure of [Cu<sub>4</sub>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-2-Cl)<sub>4</sub>(μ-DEAD)]<sub>2</sub> (**3b**), however, clearly shows that the formation of an *o*-halogen-substituted copper(I) benzoate cannot alone be responsible for the observed enhanced reactivity of carbon–halogen bonds in Hurtley type reactions.

The observed bonding mode of the alkyne in **3b** is unusual for Cu(I), and as far as we are aware, the only other example is to be found in [Cu<sub>2</sub>(TC-6,6)(μ-DEAD)] (TC-6,6 is tropocoronand-6,6, a N<sub>4</sub>-donating ligand).<sup>18</sup> In this latter complex, however, the two copper atoms are not solely brought together by the bridging alkyne ligand as in **3b** but are also held in each other's vicinity by the N<sub>4</sub>-donating ligand TC-6,6.

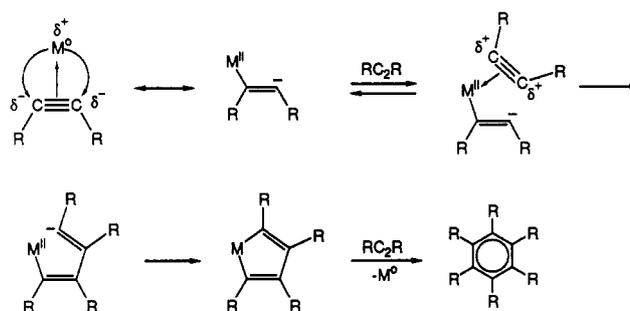
In **3b** the π-back-bonding to the acetylene appears to be smaller than in the TC-6,6 complex since the former has a shorter C≡C bond distance and larger C≡C—R bond angle deformation than the latter (Table V); this difference might be due to the better electron-accepting properties of the 2-chlorobenzoate ligand in **3b** than those of TC-6,6.

Interestingly the Cu...Cu edges bridged by the DEAD unit are longer in **3b** (2.950 Å (av)) than those in the TC-6,6 complex (2.806 (8) Å). This effect is most likely a direct consequence of the different bonding modes imposed on the copper atoms by the different ligands; i.e., benzoate units act as bridging systems whereas TC-6,6 behaves as a crown-ether-like ligand.

**Attempted Determination of the Structure of [Cu<sub>4</sub>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-2-Br)<sub>4</sub>(μ-DMAD)]<sub>2</sub> (**2c**).** Since in copper-catalyzed nucleophilic aromatic substitution reactions aryl bromides are always more reactive than their aryl chloride analogues, the elucidation of the structure of **2c** was attempted. From X-ray diffraction data the *E*<sup>2</sup>-Patterson synthesis of this bromo compound yielded the same tetrahedral arrangement of the Cu atoms as for **3b** (vide supra) and the overall structure appeared to be very similar. Unfortunately, due to strong pseudosymmetric reflections, satisfactory refinement was not possible.

**Attempted Synthesis of Dimeric Copper(I) Benzoate Alkyne Complexes.** Since the stoichiometry of tetranuclear 2:1 copper(I) benzoate:alkyne complexes **2** and **3** contrasts with that of the 1:1 complex that was reported to be the isolated product of the reaction of copper(I) benzoate with dimethyl acetylenedicarboxylate (DMAD) in methanol,<sup>5</sup> the reactions of eq 2 were repeated with use of methanol instead of diethyl ether as solvent.

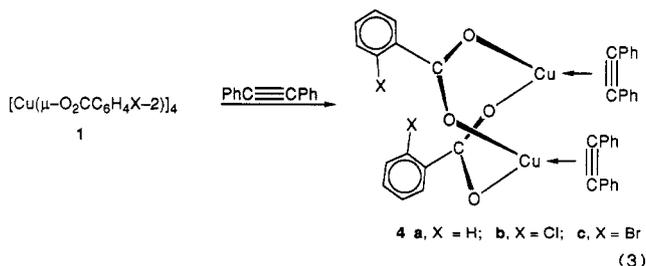
In methanol the reactant copper(I) benzoate to RC≡CR stoichiometry was found to be very critical in determining the type of product formed. When the procedure described earlier<sup>5</sup> (Cu:DMAD = 1:0.88) was followed exactly, we repeatedly obtained not a 1:1 complex of DMAD and copper(I) benzoate but a mixture of the starting compound, copper(I) benzoate, copper

**Scheme 1**

metal, and the trimerized acetylene, hexamethyl mellinate. Even the reversed addition of the reactants had no effect on the products formed in this reaction. When, however, the Cu:DMAD ratio was increased to 1:1.6, the reaction of **1a** with DMAD yielded the tetrameric copper(I) alkyne coordination compound **2a** in 60% yield.<sup>21</sup>

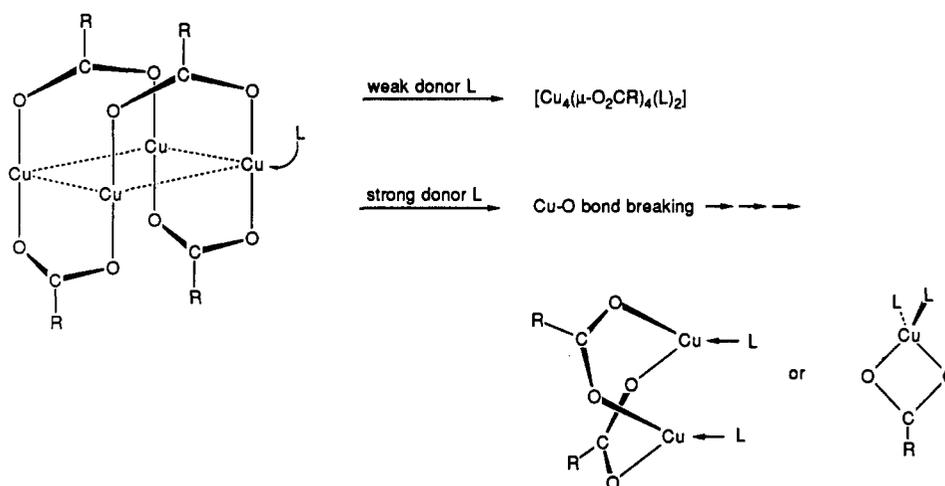
In an independent experiment isolated and purified [Cu<sub>4</sub>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(μ-DMAD)]<sub>2</sub> (**2a**) when dissolved in methanol gave an instantaneous reaction and trimerized DMAD was formed. Not unexpectedly, the reactions of copper(I) 2-halobenzoates **1b** and **1c** (which are unstable in methanol) with DMAD in methanol were unsuccessful; decomposition took place (the products were not identified).

In a further attempt to prepare a dimeric benzoate alkyne complex the reactions of [Cu(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-2-X)]<sub>4</sub> (X = Cl (**1b**), Br (**1c**)) with the less activated diphenylacetylene, PhC≡CPh, were carried out in diethyl ether and did in fact yield [Cu(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-2-X)(PhC≡CPh)]<sub>2</sub> (X = Cl (**4b**), Br (**4c**); eq 3). The



elemental analytical data for these compounds indicate that they were contaminated with some starting copper(I) benzoate even after a reaction period of 20 h. If the reaction period was prolonged to 48 h, the isolated products, which have limited thermal stability, always had a slight blue coloration most likely resulting from a thermally induced valence disproportionation reaction.

The synthesis in methanol of the complex [Cu(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)(PhC≡CPh)]<sub>2</sub> (**4a**) has been published earlier by Floriani et al.,<sup>5</sup> and their procedure affords this product in a pure form and in higher yields than obtained by us (yield 70% of impure product). Since the 2-chloro- and 2-bromo-substituted copper(I) benzoates are unstable in methanol (vide supra), the preparation of alkyne complexes by this route is not feasible.

Scheme II. Breakdown of the Tetrameric Copper(I) Benzoates under the Influence of Ligands<sup>a</sup>

<sup>a</sup>For the monomeric product other compositions are possible.

The IR spectral data of the *o*-halobenzoate complexes **4b** and **4c** are similar to those reported for the copper(I) benzoate diphenylacetylene complex **4a**, which shows a weak C≡C stretching vibration at 1980 cm<sup>-1</sup>. On the basis of the IR spectral data and the elemental analytical data we believe that complexes **4b** and **4c** also contain the well-known doubly benzoato-bridged dimeric copper(I) unit (eq 3).

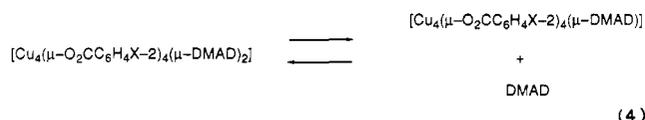
**Structure and Reactivity of the Copper(I) Benzoate Alkyne Complexes 2–4 in Solution.** At ambient temperatures under a nitrogen atmosphere the tetranuclear compounds **2** and **3** are soluble and quite stable in benzene and toluene whereas dinuclear **4** is insoluble in these solvents and decomposition occurs when dissolution in THF is attempted.

The fact that dissolution of **2** and **3** generally afforded a small amount of insoluble solid has complicated both interpretation of their NMR data and the determination of their molecular weights by cryoscopy.

The cryoscopic molecular weights we found for compounds **2** were about half that calculated for the tetranuclear copper alkyne compound (Experimental Section). This could indicate that the tetrameric complexes are dissociated into dimeric units or that on dissolution the deposition of some solid material releases alkyne ligand from the tetranuclear array.

The <sup>1</sup>H NMR data (Table I) of complexes **2** in solution provide evidence for fluxional behavior of the alkyne ligand. In benzene-*d*<sub>6</sub> at room temperature the 100-MHz <sup>1</sup>H NMR spectrum of **2a** shows a slightly broadened singlet at 2.86 ppm due to the methyl group of the DMAD ligand. The same measurement in toluene-*d*<sub>8</sub> provided a methyl signal that was even broader at 3.19 ppm; when the temperature was raised to 323 K, irreversible decomposition occurred.

These observations stimulated us to measure the NMR spectra of **2** at various temperatures on a 250-MHz spectrometer. In the case of **2a** in toluene-*d*<sub>8</sub> the methyl signal of the coordinated DMAD ligand was observed at 3.13 ppm at room temperature. Besides this resonance, there was also a broadened peak at 3.30 ppm due to free DMAD. When the temperature was lowered to 253 K, these two signals due to DMAD sharpened. These NMR results are consistent with the presence of an exchange reaction between coordinated and free DMAD, which becomes slow on the 250-MHz NMR time scale at 253 K (see eq 4). Free DMAD



can be due (i) to dissociation of alkyne from the tetranuclear copper(I) benzoate alkyne complex and (ii) to the minor decomposition on dissolution of [Cu<sub>4</sub>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(μ-DMAD)<sub>2</sub>] (**2a**) into DMAD and white insoluble solid with a DMAD to copper(I)

benzoate ratio below 1:2 (e.g. copper(I) benzoate).

<sup>1</sup>H NMR (250 MHz) spectra at 293 K of the 2-chloro-substituted compound [Cu<sub>4</sub>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-2-Cl)<sub>4</sub>(μ-DMAD)<sub>2</sub>] (**2b**) and the 2-bromo-substituted compound [Cu<sub>4</sub>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-2-Br)<sub>4</sub>(μ-DMAD)<sub>2</sub>] (**2c**) also show two slightly broadened resonances due to coordinated and free DMAD. The spectra of **2b** and **2c** were measured at low concentrations (<10<sup>-2</sup> M); on dissolution very little solid deposited and the amount of free DMAD present in solution is small. The <sup>1</sup>H NMR spectra measured at lower temperatures (253–213 K) show no significant changes other than sharpening of the signals and an upfield shift of the signal of the aromatic H(2) and the methyl DMAD protons. At 293 K the <sup>1</sup>H NMR spectra of **2b** and **2c** show shoulders on the aromatic H(2), H(4), and H(5) resonances. This suggests the occurrence of fluxional behavior, but heating these solutions led to irreversible decomposition.

The <sup>1</sup>H NMR data (Table I) for the DEAD compounds **3** showed no resonances due to the free acetylene, and in these cases the small amount of solid that deposited upon dissolution is assumed to be the compounds themselves.

It was expected that in the <sup>13</sup>C NMR spectra of complexes **2** and **3** (see the supplementary material) the *o*-halogen atom bearing C2 atom chemical shift would provide some indication for the polarization of the carbon-halogen bond in solution that would result from the proposed *o*-halogen to copper(I) interaction. The observed signals of the C2 atoms (62.3 MHz; **2b** (toluene-*d*<sub>8</sub>), δ 134.3; **2c** (benzene-*d*<sub>6</sub>), δ 121.3; **3b** (toluene-*d*<sub>8</sub>), δ 134.2; **3c** (toluene-*d*<sub>8</sub>), δ 123.1) are in the same range as that expected for the free benzoic acids, and thus, there is no interaction indicated between a halogen and a copper(I) atom. The <sup>13</sup>C NMR resonances due to the acetylene carbon atoms are close to those of the free alkyne ligand. The total effect that the bonding and back-bonding interactions of the alkyne ligands with the copper(I) atoms have on the chemical shifts is thus very small (see the supplementary material).

The reactivity of [Cu<sub>4</sub>(μ-O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(μ-DMAD)<sub>2</sub>] (**2a**) in methanol leading to the trimerization of DMAD to hexamethyl mellinate is remarkable because of its solvent dependence. Other examples of this catalytic trimerization are known.<sup>10</sup> For example, Mosely and Maitlis<sup>10a</sup> found that the reaction of Pd<sup>0</sup> and Pt<sup>0</sup> phosphine complexes with DMAD leads to the formation of hexamethyl mellinate via a sequence of steps that involve the

- (10) (a) Mosely, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169. (b) Corsico Coda, A.; Desimoni, G.; Gamba Invernizzi, A.; Quadrelli, P.; Righetti, P. P.; Tacconi, G. *Tetrahedron* **1987**, *43*, 2843. Desimoni and co-workers found that Cu(II) caused the trimerization of DMAD, but in these cases the trimerized DMAD was found to be coupled to an aryl unit. The role of Cu(II) in this reaction was not elucidated. (c) Keim, K.; Behr, A.; Röper, M. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, England, 1982; Chapter 52, p 371.

formation of a  $\pi$ -acetylene complex and a subsequent series of dipolar intermediates; the latter intermediates produce a metalacyclopentadiene, which can then react with DMAD to give hexamethyl mellinate (see Scheme I). The proposed driving force for this trimerization is the nucleophilicity of the  $d^{10}$  metal. In our case the trimerization is most likely a result of the nucleophilicity of the copper(I) metal atom and the ligating properties of the methanol solvent that may be able to break down the tetrameric copper(I) benzoate cluster of dimeric units.<sup>5,6b</sup>

When a large excess of DMAD is reacted with copper(I) benzoate, trimerization of DMAD is prevented and  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\mu\text{-DMAD})_2]$  (**2a**) is formed; presumably under these conditions the formation of dimeric copper(I) benzoate clusters is prevented.

**Reactivity of Tetrameric Copper(I) Benzoates toward Coordinating Ligands.** The formation of coordination compounds of copper(I) benzoates clearly depends on the donor strength of the ligands used.

In known reactions of copper(I) carboxylates with unsaturated compounds weak donor ligands such as benzene,<sup>11</sup> dimethyl acetylenedicarboxylate, and diethyl acetylenedicarboxylate lead to the formation of coordination complexes wherein the initial tetrameric copper(I) carboxylate unit is retained.

In contrast, reactions of copper(I) benzoates with stronger donor ligands lead to the formation of dimeric or monomeric copper(I) benzoates. For example, the reaction of copper(I) benzoate with diphenylacetylene breaks the tetrameric structure down to dimeric **4**. The  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_2$  moiety is also found when **1a** is reacted with several nitrogen donors such as isocyanides, azo compounds,<sup>12</sup> and quinoline<sup>13</sup> (which affords  $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)]_2$ ). However, when copper(I) benzoates are reacted with phosphine ligands, monomeric species are obtained.<sup>14</sup>

The reaction of a donor ligand with a copper(I) benzoate proceeds most likely via initial attack at one of the two-coordinate copper(I) atoms (see Scheme II). The donor strength of dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate is not large enough to break a Cu–O bond in tetrameric copper(I) benzoates, and initial coordination of these ligands to a copper atom, most likely via the triple bond, thus gives rise to a three-coordinate copper atom. The acetylene ligand then interacts with the opposite copper atom in the initial parallelogram and becomes a perpendicularly oriented bridging unit. A subsequent or concomitant complexation of another acetylene unit leads to formation of the complexes **2** and **3**.

### Conclusions

The molecular structure of  $[\text{Cu}_4(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-Cl})_4(\mu\text{-DEAD})_2]$  (**3b**) and solution studies clearly show no evidence for an interaction between the copper(I) atom and the *o*-halogen atom. Therefore, the observed enhanced reactivity of the carbon–halogen bond in the Hurtley reaction cannot be ascribed solely to the formation of a copper(I) 2-halobenzoate compound.

In our reaction studies of copper(I) benzoates with several donor systems it is found that the solvents that are used in the Hurtley reaction (i.e. water, methanol, or the conjugated acids of the  $\beta$ -dicarbonyl nucleophile) are able to break down the tetranuclear array into smaller aggregates; this knowledge is of major importance for the understanding of the reactive intermediates in the Hurtley reactions.<sup>13,20</sup>

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**Registry No.** **1a** (coordination compound entry), 62914-01-6; **1a** (salt entry), 14604-51-4; **1b** (coordination compound entry), 121619-88-3; **1b** (salt entry), 50671-63-1; **1c** (coordination compound entry), 121619-89-4; **1c** (salt entry), 121619-96-3; **2a**, 121619-90-7; **2b**, 121619-91-8; **2c**, 121619-92-9; **3a**, 121619-93-0; **3b**, 121619-94-1; **3c**, 121619-95-2; **4b**, 121619-97-4; **4c**, 121619-98-5; DMAD, 762-42-5; DEAD, 762-21-0;  $\text{PhC}\equiv\text{CPh}$ , 501-65-5;  $\text{C}_6(\text{CO}_2\text{Me})_6$ , 6237-59-8.

**Supplementary Material Available:** <sup>13</sup>C NMR data (Table SI), fractional coordinates of the hydrogen atoms and isotropic thermal parameters (Table SII), anisotropic thermal parameters (Table SIII), bond distances of the non-hydrogen atoms (Table SIV), bond distances of the hydrogen atoms (Table SV), bond angles of the non-hydrogen atoms (Table SVI), and bond angles of the hydrogen atoms (Table SVII) (10 pages); a listing of structure factors (Table SVIII) (27 pages). Ordering information is given on any current masthead page.

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