

Full papers

Dinuclear copper(I) benzoato quinoline complexes as intermediates in the copper–quinoline decarboxylation reaction

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Abstract. The reaction of both the novel mixed trinuclear organo-organic copper(I) species $[\text{Cu}_3(\text{C}_6\text{H}_2\text{Me}_{3-2,4,6})(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]$ (**1**) and $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$ (**2a**) with quinoline in toluene or diethyl ether yields the dimeric 1:2 copper/quinoline complex $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$ (**3a**). The reactions of methyl-substituted copper(I) benzoates, $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)]_4$ ($x = 2$, **2b**; $x = 3$, **2c**; $x = 4$, **2d**), with quinoline in toluene or diethyl ether, however, afford the 1:1 copper/quinoline complexes $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)_2]$ ($x = 2$, **4b**; $x = 3$, **4c**; $x = 4$, **4d**).

The structure of complex **4b**, determined by a single-crystal X-ray diffraction study, shows a dicopper(I) unit doubly bridged by two benzoato units $[\text{Cu1}\dots\text{Cu1}^* = 2.667(1) \text{ \AA}]$. At each copper site, the Cu–O bonds to the bridging benzoato groups differ considerably $[\text{Cu1–O1} = 1.923(5) \text{ \AA}$; $\text{Cu1–O2}^* = 2.134(5) \text{ \AA}]$. Coordination of a quinoline at each copper site $[\text{Cu1–N1} = 1.952(5) \text{ \AA}]$ produces a distorted trigonal arrangement.

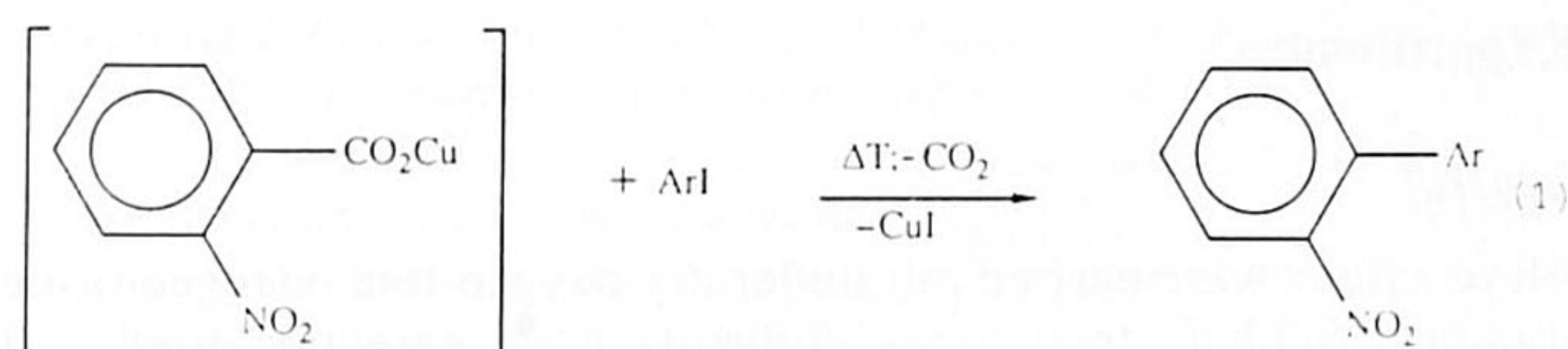
Crystallization of the 1:2 copper–quinoline complex **3a** led to formation of crystals of the dimeric 1:1 copper/quinoline complex $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)]_2$, **4a**. The structure of **4a** is similar to that of **4b** $[\text{Cu1}\dots\text{Cu1}^* = 2.638(2) \text{ \AA}$; $\text{Cu1–O1} = 1.945(6) \text{ \AA}$; $\text{Cu1–O2}^* = 2.107(6) \text{ \AA}$; $\text{Cu1–N1} = 1.939(7) \text{ \AA}]$. Since complexes **3** and **4** can be expected to be similar to the intermediates formed in the copper–quinoline decarboxylation reaction, the reactivity of **3** and **4** at elevated temperatures in non-coordinating solvents has been studied. It was found that the decarboxylation reaction requires more than one equivalent of quinoline per copper atom. An improved mechanism is presented for the copper–quinoline decarboxylation reaction involving dinuclear copper(I) complexes as intermediates.

Introduction

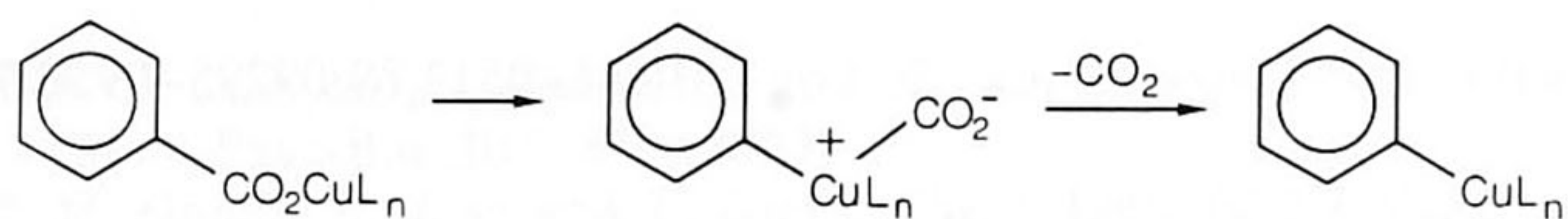
The copper–promoted decarboxylation reaction of benzoic acids in quinoline¹, *i.e.* the copper–quinoline decarboxylation reaction, has been thoroughly investigated by many research groups and it is generally accepted that reactive copper(I) intermediates are involved. The formation of mixed biaryls from this reaction as reported by Nilsson and coworkers² (Eqn. 1) indicates that an organocopper(I) intermediate is formed during the reaction sequence. Further evidence for such intermediates comes from the isolation of (pentafluorophenyl)copper(I) from the low-temperature de-

carboxylation reaction of copper(I) pentafluorobenzoate (Eqn. 2)³.

A thorough mechanistic study of the decarboxylation of several pure copper(I) benzoates in pyridine and quinoline has been published by Cohen and coworkers⁴, who proposed a mechanism which involves insertion of a copper(I), with associated ligands, into the carbon–carbon bond of the carboxylate to form a copper(III) intermediate which was thought to be capable of rapid conversion into a copper(I) intermediate by loss of carbon dioxide (see Scheme 1).

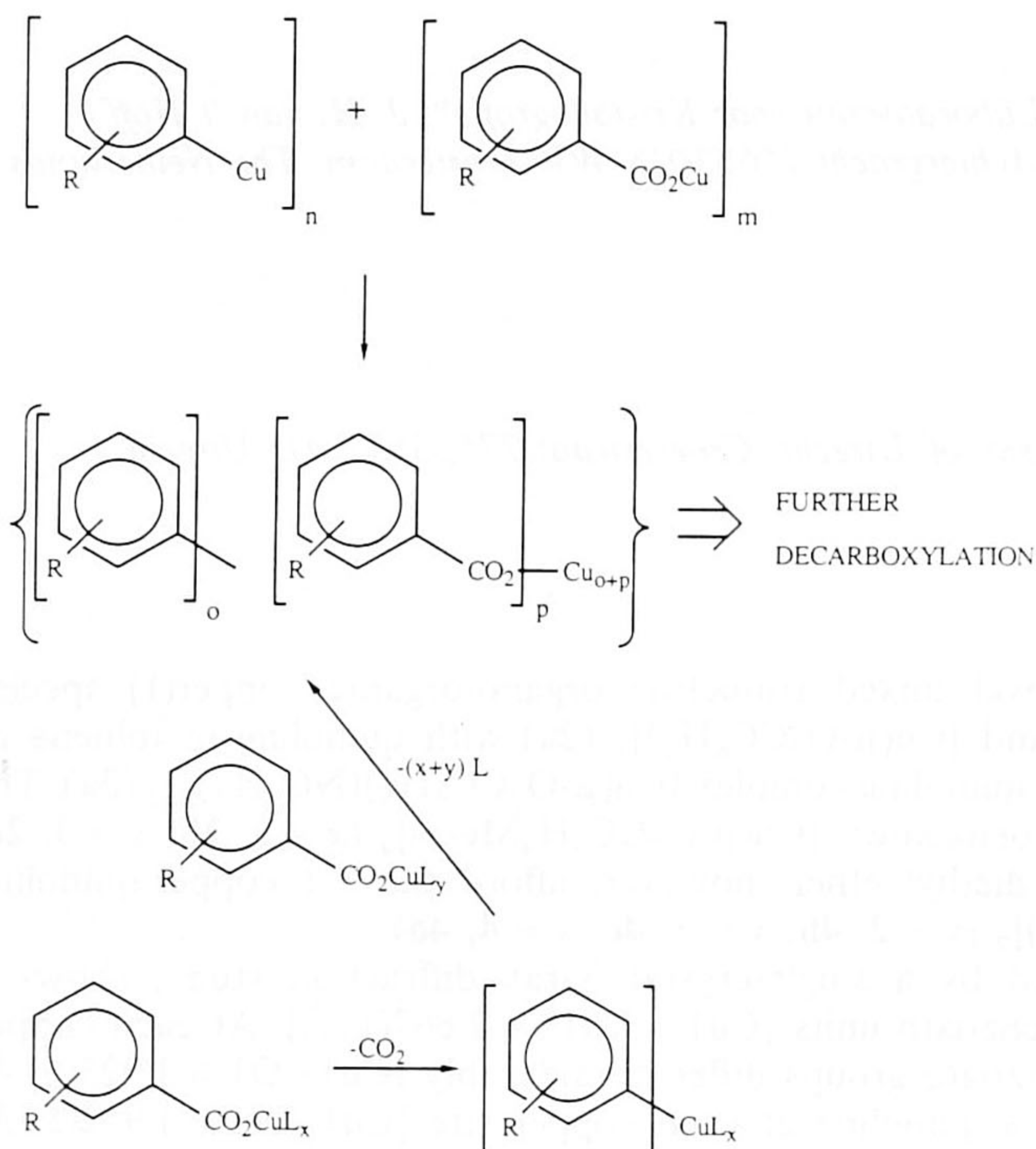


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Scheme 1. Proposed intermediates in the copper-quinoline decarboxylation reaction⁴.

Recently, we have shown that the reaction of pentameric mesitylcopper(I) and tetrameric copper(I) benzoate results in the formation of a novel mixed trinuclear organo-organic copper(I) species $[\text{Cu}_3(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]$ (**1**)⁵. Mixed organo-organic copper(I) compounds of this type can be seen as models for the intermediates which may be present during the copper-assisted decarboxylation reaction of benzoic acids (see Scheme 2).



Scheme 2. *m* and *n* indicate the degree of association, e.g. for tolylcopper *n* = 4; *o* and *p* indicate the number aryl and benzoate groups present in the mixed aggregate.

Because of our interest in copper-promoted reactions, we have studied the reaction of trinuclear **1** and of several copper(I) benzoates with quinoline. From these reactions, it has been possible to isolate and characterize several complexes containing a dicopper(I) unit doubly bridged by two benzoates wherein the copper(I) coordination sphere is completed by one or two quinoline fragments. Two of the isolated complexes have been structurally characterized by X-ray crystallography.

Since the isolated copper(I) benzoate quinoline complexes can be expected to be similar to the intermediates formed in copper-quinoline decarboxylation reactions, the reactivity of these copper(I) complexes has been studied at elevated temperatures in non-coordinating solvents. Based on our results, we present an improved mechanism for the copper-quinoline decarboxylation reaction involving dinuclear copper(I) complexes as intermediates.

Experimental

General

All reactions were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were carefully dried and

distilled prior to use. Starting materials are commercially available (Janssen Chimica). $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$ (**2a**) was synthesized according to a literature procedure⁶. The methyl-substituted copper(I) benzoates, $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)]_4$ (*x* = 2, **2b**; *x* = 3, **2c**; *x* = 4, **2d**), were synthesized via a similar route or using a method developed by ourselves⁵.

¹H NMR spectra were recorded on a Bruker AC 100 spectrometer. IR spectra (Nujol) were recorded on a Perkin-Elmer 283 spectrometer. Cryoscopic molecular weight determinations were carried out in benzene under dry oxygen-free nitrogen. The degree of association was measured in a concentration range (based on the monomeric unit) of 10^{-2} – 10^{-1} mol/l. Elemental analyses were carried out by the Analytical Section of the Institute of Applied Chemistry TNO, Zeist, The Netherlands.

Analysis of the organic products after the decarboxylation procedure was carried out using a combination of gas chromatography-mass spectrometry (GC-MS) and gas-liquid chromatography (GLC). The GC-MS spectra were recorded on a Kratos MS 80 combined gas chromatograph-mass spectrometer. The mass spectra were recorded at an ionizing voltage of 40 eV. GLC analyses were performed on a Varian Aerograph 144010-01 gas chromatograph equipped with a Shimadzu Chromatopac C-R2AX integrator. Yields were calculated from peak areas using internal standard techniques. The relative response factors were calculated based on the effective carbon contributions of the different carbon atoms⁷ present in the products.

Reaction of $[\text{Cu}_3(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]$ with quinoline

Quinoline (5 ml, 42.2 mmol) was added to a solution of $[\text{Cu}_3(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]$ (1.106 g, 2 mmol) in toluene (10 ml). Immediately, an orange suspension was formed. This reaction mixture was stirred for 2 h after which the yellow precipitate was filtered off and washed with toluene (3 × 5 ml) and hexane (3 × 10 ml). Yield 1.33 g of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$, **3a** (75%).

Synthesis of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$ (**3a**)

Quinoline (1.30 ml, 11.0 mmol) was added to a toluene suspension (20 ml) of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$ (**2a**) (927 mg, 5 mmol, based on the monomeric unit). Immediately, a red solution was formed which turned, after a few minutes, into an orange suspension. This reaction mixture was stirred for 2 h after which the yellow precipitate was filtered off and washed with toluene (2 × 5 ml) and hexane (3 × 10 ml). Yield 1.77 g (80%) of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$, **3a**. Elemental analysis: **3a** $\text{C}_{50}\text{H}_{38}\text{Cu}_2\text{N}_4\text{O}_4$ (885.94) calcd.: C 67.78, H 4.32, Cu 14.35, N 6.32, O 7.22; found: C 67.73, H 4.32, Cu 14.48, N 6.27, O 7.21%. Molecular weight found: 462. IR (Nujol; 1500–1700 cm^{-1}): 621(w), 1599(s), 1559(s), 1504(m) cm^{-1} .

The synthesis of **3a**, carried out in diethyl ether, leads to immediate formation of the orange suspension and ca. 10% higher yields.

Synthesis of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)_2]_2$ (*x* = 2, **4b**; *x* = 3, **4c**; *x* = 4, **4d**)

Quinoline (1.30 ml, 11.0 mmol) was added to a toluene suspension (20 ml) of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)]_4$ (997 mg, 5 mmol, based on the monomeric unit) resulting in the formation of a red solution from which, after a few minutes, a yellow-orange solid precipitated. The reaction mixture was stirred for 2 h after which the precipitate was filtered off and washed with toluene (2 × 5 ml) and hexane (3 × 10 ml). Yield 60–70% of yellow-orange $[\text{Cu}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)_2]_2$. Elemental analysis for $\text{C}_{34}\text{H}_{28}\text{Cu}_2\text{N}_2\text{O}_4$ (655.68) calcd.: C 62.28, H 4.30, Cu 19.38, N 4.27, O 9.76; **4b** found: C 62.81, H 4.60, Cu 17.32, N 4.77, O 8.85; **4c** found: C 61.71, H 4.49, Cu 19.15, N 4.12, O 9.45; **4d** found: C 60.44, H 4.54, Cu 19.88, N 3.87, O 10.47%. ¹H NMR (benzene-*d*₆, δ ppm): **4b**, δ 2.81 (s, 2-Me); **4c**, δ 2.13 (s, 3-Me); **4d**, δ 2.05 (s, 4-Me). Molecular weight found: **4c**, 636; **4d**, 503. IR (Nujol; 1500–1700 cm^{-1}): **4b**, 1609(w), 1552(s), 1527(m), 1501(s) cm^{-1} ; **4c**, 1618(w), 1608(w), 1593(s), 1564(br, s), 1502(s) cm^{-1} ; **4d**, 1618(vw), 1593(s), 1589(s), 1554(s), 1538(m), 1505(s) cm^{-1} .

The reaction could be carried out in diethyl ether (*vide supra*). Crystals of **4b** could be obtained by slow distillation of hexane onto the filtrate of the reaction mixture.

Attempted crystallization of [Cu(μ -O₂CC₆H₅)(NC₉H₇)₂]₂ (3a)

Attempts to obtain crystals of **3a** were unsuccessful. The methods tried were (i) distillation of hexane onto solutions of **3a**, (ii) cooling of saturated solutions of **3a** and (iii) sublimation of **3a** at low pressure (10⁻⁴ mm Hg, 70°C). The latter method resulted in the dissociation of quinoline affording **2a**; the first equivalent of quinoline was lost within 3 h, while dissociation of the remaining quinoline took 48 h.

In one case, yellow crystals were obtained by allowing the combined washings of the reaction mixture of **3a** to stand for 2 days. The crystals, isolated by decanting the solution and subsequent washing with hexane (2 × 10 ml), were shown not to be **3a** but rather [Cu(μ -O₂CC₆H₅)(NC₉H₇)₂]₂, **4a**.

Reactions of copper(I) benzoates with 8-methylquinoline

When copper(I) benzoates **2** were treated with 8-methylquinoline in toluene, no reaction occurred and the copper(I) benzoates were recovered quantitatively and identified on the basis of their IR spectra.

Structure determination and refinement of 4a and 4b

The crystals selected for study were mounted in glass capillaries sealed under nitrogen. Crystals of [Cu(μ -O₂CC₆H₅)(NC₉H₇)₂]₂ (**4a**) C₃₂H₂₄Cu₂N₂O₄, are monoclinic, space group *C* 2/c, *Z* = 4, *a* = 20.553(4), *b* = 10.039(2), *c* = 13.759(3) Å, β = 109.75(3)°, *V* = 2672 Å³, μ (CuK α) = 22.59 cm⁻¹, *d*_{calcd.} = 1.56 g·cm⁻³.

1083 intensities ($\theta \leq 45^\circ$; *h* 0 to 17, *k* 0 to 9, *l* 0 to 12) were measured on a NONIUS CAD4 diffractometer employing graphite-monochromatized CuK α radiation. 763 were above the 2.5 $\sigma(I)$ level and were treated as observed. Crystals dimensions: 0.5 × 0.2 × 0.1 mm. The structure was solved by means of Direct Methods using the symbolic addition program set SIMPEL⁸. Block-diagonal least-squares refinement converged to an *R* value of 0.044 (*R*_w = 0.061). An empirical absorption correction (DIFABS⁹) was applied. A weighting scheme $w = 1/(9.82 + F_o + 0.0131 F_o^2)$ was used and the anomalous scattering of Cu was taken into account¹⁰. H atoms were found in a ΔF synthesis. All non-hydrogen atoms were treated anisotropically and the H atoms isotropically. The programs used were from XRAY 76¹¹.

Crystals of [Cu(μ -O₂CC₆H₄Me-2)(NC₉H₇)₂]₂ (**4b**) C₃₄H₂₈Cu₂N₂O₄ are orthorhombic, space group *Pnca*, *Z* = 4, *a* = 14.085(1), *b* = 20.465(2), *c* = 10.024(1) Å, *V* = 2889.4(10) Å³, μ (CuK α) = 21.1 cm⁻¹, *d*_{calcd.} = 1.51 g·cm⁻³.

2973 intensities ($\theta \leq 65^\circ$; *h* 0 to 16, *k* 0 to 24, *l* 0 to 11; crystal dimensions: 1.1 × 0.5 × 0.15 mm) were measured on a NONIUS CAD4 diffractometer employing graphite-monochromatized CuK α radiation. 999 were below the 2.5 $\sigma(I)$ level and were treated as unobserved. The structure was solved by means of the heavy-atom method. Refinement proceeded by means of block-diagonal least-squares calculations. After applying an empirical absorption correction (DIFABS⁹), the H atoms were indicated in a ΔF synthesis and included in the refinement with isotropic temperature parameters. Continued refinement converged to an *R* value of 0.059 (*R*_w = 0.101). A weighting scheme $w = 1/(8.2 + F_o + 0.0046 F_o^2)$ was applied and the anomalous scattering of Cu was taken into account¹⁰. The programs used were from XRAY 76¹¹.

Decarboxylation procedure

To 10 ml of a decarboxylation solvent (toluene, naphthalene or decalin) at reflux in a three-necked round-bottom flask equipped with a condenser was added 3.3 mmol of the copper(I) compound (based on the monomeric unit). When the influence of a second equivalent of quinoline on the decarboxylation reaction was studied, 1.1 equivalent of quinoline per copper atom was added to the decarboxylation solvent before it was brought to reflux. The evolved carbon dioxide in these reactions was collected by sweeping a slow stream of nitrogen over the reaction mixture through the condenser and a cold trap, cooled by a mixture of dry-ice and ethanol, into two Ascarite tubes where the carbon dioxide was absorbed.

Analysis of products from the decarboxylation procedure

The reaction mixtures were only analysed for the successful decarboxylation reactions using naphthalene as solvent. The reaction mixture was added to diethyl ether; all components except some copper salts dissolved. This ethereal suspension was extracted with 1 N hydrochloric acid, washed with water, and the ethereal solution dried over anhydrous MgSO₄ and concentrated to provide the neutral fraction. The aqueous acid extract was neutralized with sodium bicarbonate, made slightly basic with concentrated ammonium hydroxide, and then extracted with diethyl ether. The ether extracts were dried over anhydrous MgSO₄ and concentrated to provide the basic fraction.

The qualitative and quantitative analysis of the neutral fraction was unsuccessful because of the very large quantity of naphthalene present. For quantitative analysis of the basic fraction, durene was added as internal standard. In every reaction, at least 90% of the quinoline fragments were recovered in the basic fraction.

The quantitative analysis of a reaction mixture was performed using gas-liquid chromatography (GLC), using a CP-Sil 5 column (Chrompack, 25 m × 0.22 mm × 0.32 μ). The nitrogen flow rate was 6 ml/min; the initial column temperature was 80°C with a programmed rise of 6°C/min to 300°C. The product percentages found (see Table III) have an accuracy of 5 rel. %. The qualitative GC/MS analyses were conducted on a BP 1 column (S.G.E.; flow 2 ml/min; split various) using a comparable time program.

Combined GLC and GC-MS data of the basic fraction products: compound, retention time, m/z (%; fragment):

Assignments are generally made by comparison with literature data⁴; Q = quinolyl⁺ = C₉H₆N⁺; N = naphthyl⁺ = C₁₀H₇⁺; the *m/z* peaks with a relative intensity below 10 are omitted, unless important.

2-Benzoylquinoline, 25.1 min, 233(38; M⁺); 232(18; M⁺-1), 205(45; M⁺-CO), 204(100; M⁺-HCO), 128(28; Q), 105(46; M⁺-C₆H₅-CO), 77(49; C₆H₅).

2-(2-Methylbenzoyl)quinoline, 25.5 min, 247(8; M⁺), 246(18; M⁺-1), 233(13; M⁺-CH₂), 232(62; M⁺-CH₃), 220(8; M⁺-HCN), 219(31; M⁺-CO), 218(100; M⁺-HCO), 217(26; M⁺-H₂CO), 204(53; M⁺-CO-CH₃), 128(17; Q), 119(17; M⁺-Q), 91(14; γ H₇), 76(13; C₆H₄).

2-(3-Methylbenzoyl)quinoline, 25.6 min, 247(21; M⁺), 246(10; M⁺-1), 232(5; M⁺-CH₃), 220(7; M⁺-HCN), 219(36; M⁺-CO), 218(100; M⁺-HCO), 217(16; M⁺-H₂CO), 204(54; M⁺-CO-CH₃), 128(18; Q), 119(13; M⁺-Q), 91(21; C₇H₇).

2-(4-Methylbenzoyl)quinoline, 26.9 min, 247(21; M⁺), 246(12; M⁺-1), 232(9; M⁺-CH₃), 220(5; M⁺-HCN), 219(30; M⁺-CO), 218(100; M⁺-HCO), 204(63; M⁺-CO-CH₃), 128(17; Q), 119(29; M⁺-Q), 91(35; C₇H₇), 65(19), 57(22).

Isomer A of naphthylquinoline (NQ-A), *8-naphthylquinoline**, 30.0 min, 255(49; M⁺), 254(100; M⁺-1), 253(20; M⁺-2), 252(13; M⁺-3), 226(5; M⁺-2H-HCN), 127(11; N).

Isomer B of naphthylquinoline (NQ-B), *2-naphthylquinoline**, 29.0 min, 255(99; M⁺), 254(100; M⁺-1), 226(21; M⁺-2H-HCN), 219(24), 218(80), 204(45), 128(20; Q), 127(32; N), 91(31; C₇H₇), 65(13), 43(14).

Isomer C of naphthylquinoline* (NQ-C, 1.7 min, 255(100; M⁺), 254(82; M⁺-1), 253(24; M⁺-2), 127(13; N), 128(7; Q).

2,2'-Diquinolyl ether, 32.7 min, 272(43; M⁺), 271(100; M⁺-1), 255(15; M⁺-OH), 254(12; M⁺-H₂O), 243(18; M⁺-2H-HCN), 128(11; Q).

* The tentative assignment to 8-naphthylquinoline and 2-naphthylquinoline is based on the parent-to-parent - 1 peak ratio. For 8-naphthylquinoline, this ratio is 49:100 (indicative of the easy five-ring formation in the M⁺-1 fragment) whereas this ratio is 99:100 for 2-naphthylquinoline (indicative of the more difficult four-ring formation in its M⁺-1 fragment). In the case of naphthylquinoline-C, the naphthyl fragment is coupled further away from the quinoline nitrogen atom, although the exact coupling place cannot be assigned.

Results and discussion

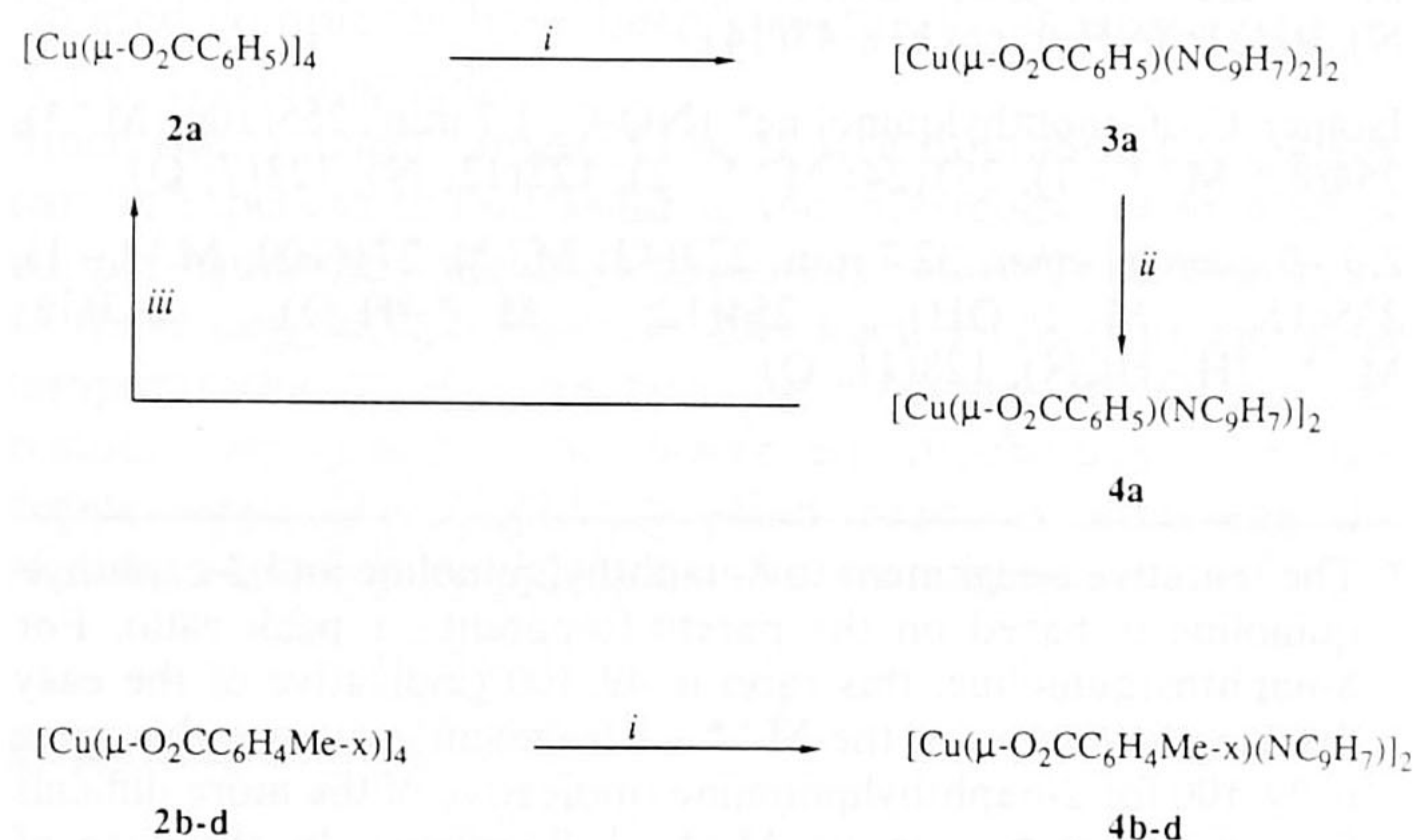
Synthesis and characterization of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_n]_2$ ($n = 2$, **3a**; $n = 1$, **4a**) and $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)_2]_2$ ($x = 2$, **4b**; $x = 3$, **4c**; $x = 4$, **4d**)

The reaction of the novel trinuclear mixed organo-organic copper(I) species $[\text{Cu}_3(\text{C}_6\text{H}_2\text{Me}_{3-2,4,6})(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]$ (**1**) and of $\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4$ (**2a**) with quinoline in toluene yields a yellow complex, $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$ (**3a**). In contrast, the reaction of *o*-, *m*- and *p*-methyl-substituted copper(I) benzoates $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)]_4$ ($x = 2$, **2b**; $x = 3$, **2c**; $x = 4$, **2d**) with quinoline yields the yellow-orange dimeric 1:1 complexes $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)]_2$ (**4b**, **4c**, **4d**). The copper(I) benzoates **2**, however, do not react at ambient temperature with the bulkier ligand 8-methylquinoline.

The solids **3a** and **4b-d** turn slowly green when exposed to air (within 24 h). Compounds **3a** and **4b-d** are slightly soluble in aromatic solvents in which they are extremely sensitive towards oxygen. Based on previous results^{12,13}, it was anticipated that **3a** and **4b-d** would have dimeric structures. Complex **3a** differs from complexes **4** in that the stoichiometry between the copper(I) benzoate unit and quinoline (established by elemental analysis) is 1:2 and not 1:1 as in the latter (see Scheme 3).

The ¹H NMR spectra of **3a** and **4** (benzene-*d*₆) confirmed these stoichiometries with the chemical shifts of both the benzoate and quinoline systems being found to be similar to those of the free ligands; the arylbenzoate resonances and those of H(3)–H(8) of the quinoline fragment fall together in the region 6.5–8.3 ppm, with the H(2) proton at lower field.

IR absorption spectra of **3a** and **4** (Nujol mull) all show similar bands in the region 1500–1700 cm⁻¹ and, although they confirm the presence of carboxylate and quinoline groups, they do not provide suitable additional information for structural characterization. The UV absorption spectra of **3a** and **4** were also not particularly informative; all species produced spectra with a strong broad band (due to the quinoline ligand) and a shoulder at *ca.* 380 nm, possibly due to MLCT (metal-to-ligand charge transfer) interactions. To determine the nuclearity of complexes **3a** and **4b-d**, cryoscopic molecular weight determinations were carried out in benzene (10⁻²–10⁻¹ mol/l). The value of 636 Dalton obtained for **4c** is in good agreement with the dimeric formulation $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}3)(\text{NC}_9\text{H}_7)]_2$ (MW calcd. 656) and provides strong evidence that this species exists as an undissociated dimer in solution. However, the molecular weight determined for **4d** (503) is significantly lower than



that anticipated for the dimer (MW calcd. 656) and the situation here is clearly ambiguous. Furthermore, measurements on **3a**, which was also anticipated to have a dimeric structure, gave a molecular weight value of 462 Dalton which is close to that of 443 calculated for the monomeric structure $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)]_2$.

To assist in our understanding of the different quinoline benzoate ratios in **3a** and **4** and in order to gain further insight into the solution behaviour of these species it was realized that X-ray crystallographic structural analyses were necessary. We were successful in preparing suitable crystals of **4b**.

The apparently weak coordination of quinoline in **3a** has thwarted our efforts to obtain crystalline samples. For example, attempted sublimation (70° C, 10⁻⁴ mm Hg) led to formation of **2a** through quinoline loss (Scheme 3; see Experimental). In one case, during the attempted crystallization of **3a**, a small number of yellow crystals of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)]_2$, **4a**, with a 1:1 stoichiometry between the copper(I) benzoate unit and the quinoline ligand, were obtained (Scheme 3; see Experimental).

Molecular geometry of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)]_2$, **4a**, and of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}2)(\text{NC}_9\text{H}_7)]_2$, **4b**

The crystal structure of compound **4a**, refined to *R* = 0.044 for 763 reflections, consists of the packing of 4 discrete dinuclear molecules in a monoclinic unit cell. The molecular geometry of **4a**, along with the adopted numbering scheme, is shown in Fig. 1 and relevant interatomic distances and angles are presented in Table I.

Complex **4a** comprises a central dinuclear copper(I) unit $[\text{Cu1}-\text{Cu1}^* = 2.638(2) \text{ \AA}]$ which is bridged by two O-bonded benzoate ligands. The planar-trigonal arrangement around each copper atom is completed by the N-donor coordination of a quinoline ligand. There is some distortion of this trigonal arrangement $[\text{N1}-\text{Cu1}-\text{O1} = 147.9(3)^\circ; \text{N1}-\text{Cu1}-\text{O2}^* = 104.9(3)^\circ; \text{O1}-\text{Cu1}-\text{O2}^* = 107.0(2)^\circ]$ due to steric hinderance between the phenylene ring of the quinoline ligand, which is oriented \perp to the Cu...Cu axis, and the adjacent benzoate ligand. Based on the structure shown in Fig. 1, it can be anticipated that the alternative arrangement of the quinoline ligand, parallel to the Cu...Cu axis, is not possible.

An interesting structural feature of **4a** is that the Cu1–O2* bond length of 2.107(6) Å is considerably longer than the

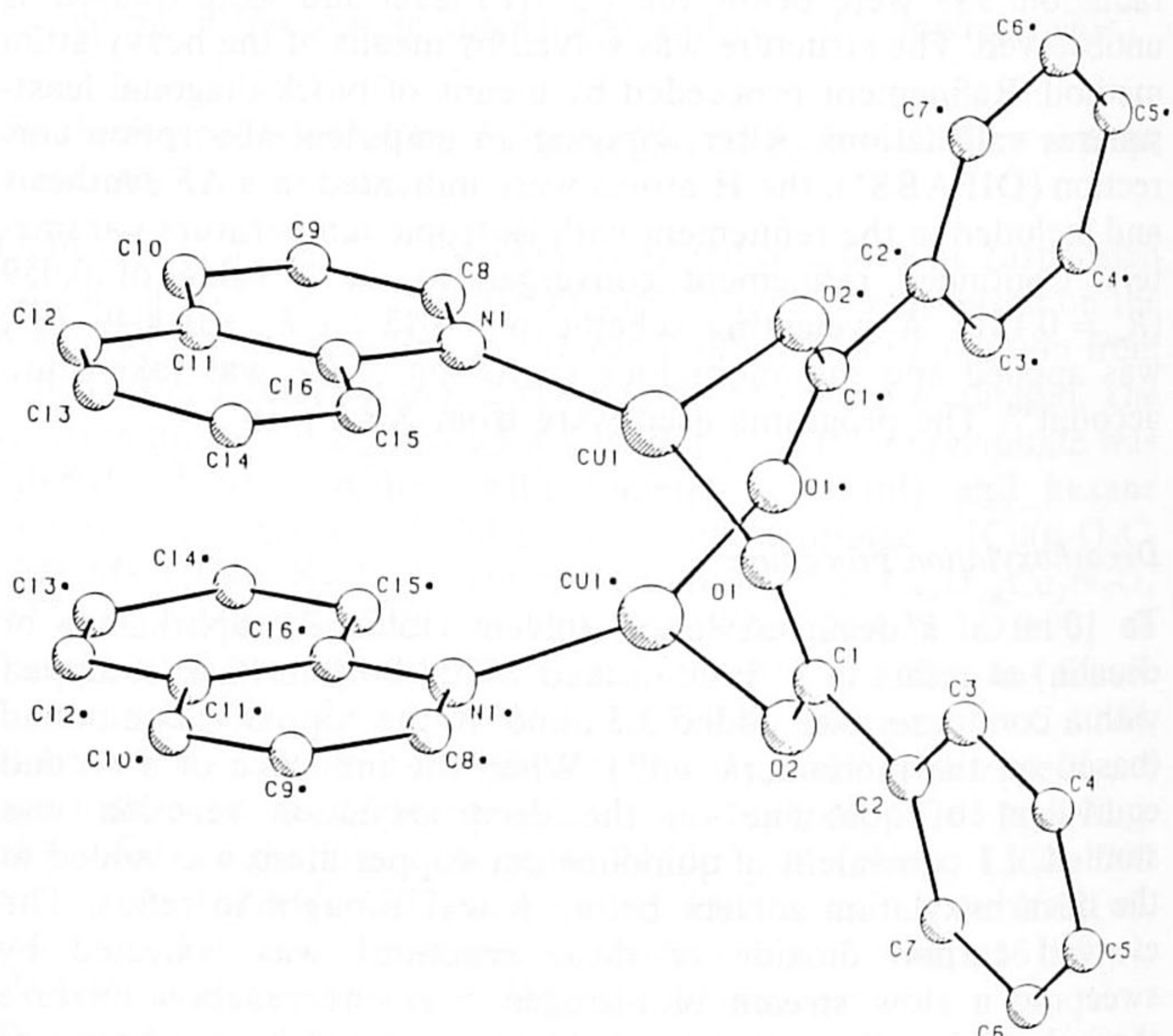
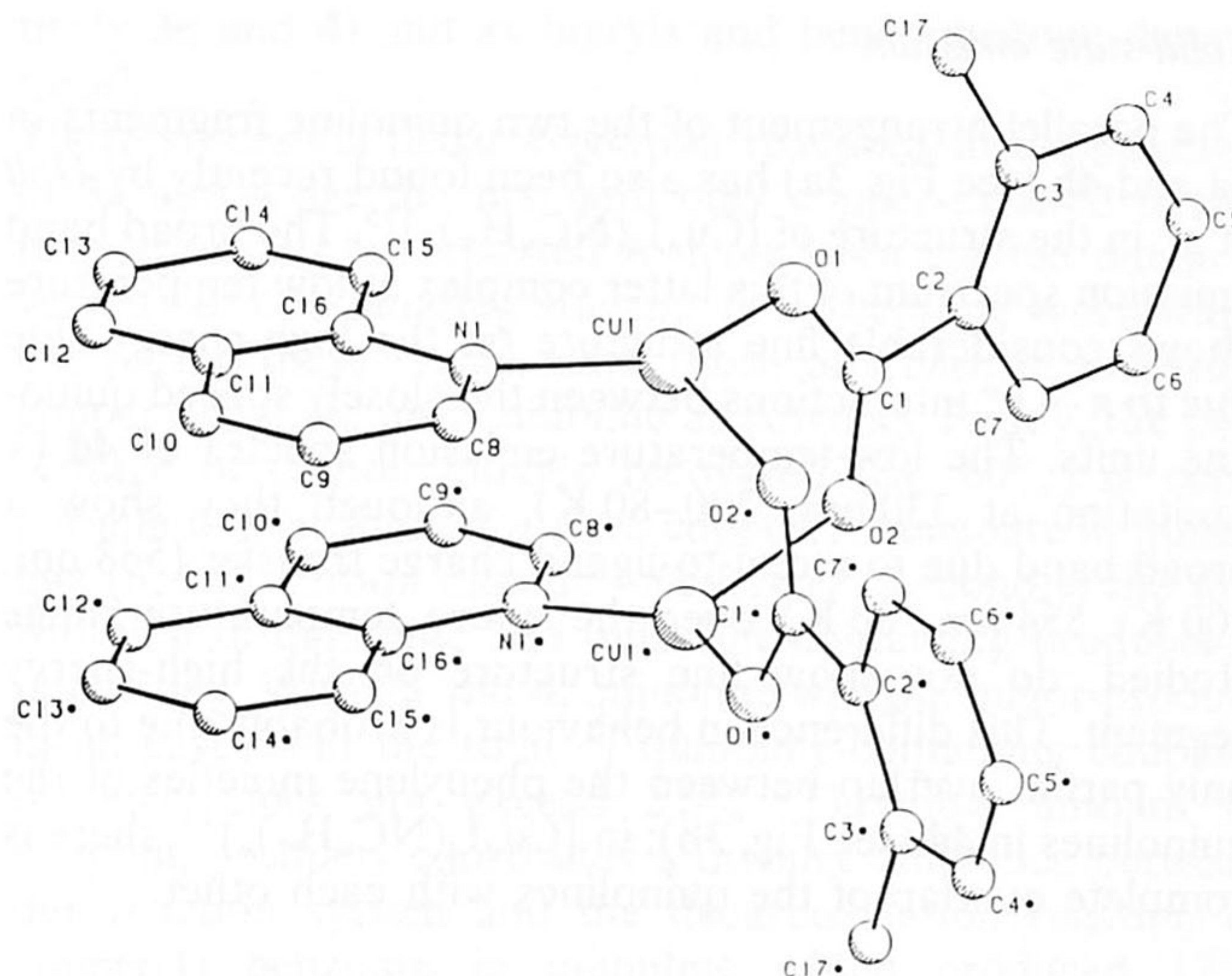


Fig. 1. PLUTO drawing of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)]_2$ (**4a**) showing the adopted numbering scheme.

Table I Selected interatomic distances and angles of **4a** and **4b**.

	4a	4b
<i>(a) Distances (Å)</i>		
Cu1–Cu1*	2.638(2)	2.667(1)
Cu1–N1	1.939(7)	1.952(5)
Cu1–O1	1.945(6)	1.923(5)
Cu1–O2*	2.107(6)	2.134(5)
C1–O1	1.272(10)	1.277(8)
C1–O2	1.249(8)	1.240(8)
C1–C2	1.492(12)	1.506(8)
<i>(b) Angles (°)</i>		
N1–Cu1–O1	147.9(3)	147.1(2)
N1–Cu1–O2*	104.9(3)	100.3(2)
O1–Cu1–O2*	107.0(2)	112.5(2)
Cu1–N1–C8	117.7(5)	119.2(4)
Cu1–N1–C16	124.2(6)	123.3(4)
C8–N1–C16	117.2(7)	117.2(5)
Cu1–O1–C1	121.1(5)	122.2(4)
Cu1*–O2–C1	124.4(6)	124.8(4)
C2–C1–O1	117.2(6)	118.5(5)
C2–C1–O2	117.5(8)	117.6(6)
O1–C1–O2	125.3(8)	123.9(6)
<i>(c) Torsion angles (°)</i>		
O1–C1–C2–C3	12(1)	12(1)
O2–C1–C2–C7	11(1)	9(1)

Fig. 2. PLUTO drawing of $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-2})(\text{NC}_9\text{H}_7)]_2$ (**4b**) showing the adopted numbering scheme.

Cu1–O1 bond length of 1.945(6) Å. This difference does not appear to be caused by intermolecular interference since all interatomic non-bonding contact distances involving the copper atoms are larger than 3.26 Å. Therefore, this structural feature is almost certainly a direct reflection of an asymmetric bonding mode of the benzoate ligands.

The crystal structure of compound **4b**, refined to $R = 0.059$ for 1974 reflections, consists of the packing of 4 discrete dinuclear molecules in an orthorhombic unit cell. The molecular geometry of **4b**, along with the adopted numbering scheme, is shown in Fig. 2 and relevant interatomic distances and angles are presented in Table I.

Complex **4b**, like **4a**, has a dimeric copper(I) benzoate structure [Cu1...Cu1* = 2.667(1) Å] and its basic structural features, *i.e.* trigonal copper(I) coordination realized by bridge bonding of two benzoates and N-donor bonding of the quinolines, closely resemble those of **4a**.

There are, however, some minor differences. In **4b**, the Cu1–O2* bond length of 2.134(5) Å is somewhat longer than that of the corresponding bond length in **4a** [2.107(6) Å], while the Cu1–O1 bond in **4b** [1.923(5) Å] is slightly shorter than the corresponding bond in **4a** [1.945(6) Å]. Also, the distortion of trigonal geometry

around copper in **4b** [N1–Cu1–O1 = 147.1(2)°; N1–Cu1–O2* = 100.3(2)°; O1–Cu1–O2* = 112.5(2)°] is more pronounced than in **4a** (*vide supra*).

In the structures of both **4a** and **4b**, the benzoate aryl ring and the CO₂ group are almost coplanar and, therefore, the introduction of an *o*-methyl group in the latter compound is seen to have little structural influence. In both complexes, the two quinoline fragments lie almost parallel to each other (see Figure 3a) and the significance of this feature is discussed later.

Complexes **4a** and **4b** are new examples of dimeric copper(I) species containing a dinuclear copper(I) unit which is doubly bridged by benzoate ligands. Compared to other copper(I) species of this type, they show some interesting features (see Table II). For instance, the Cu...Cu distances in **4a** and **4b** are the shortest so far found for this type of complex. Secondly, the Cu1–O2* distances in **4a** and **4b** are considerably longer than those found in other known structures with doubly bridging benzoate units. This indicates that these Cu1–O2* bonds are somewhat weaker than the Cu1–O1 bonds. The Cu1–O2* distances in **4a** and **4b** are even longer than those involving the tetracoordinated copper(I) atom in $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2(\text{CNC}_6\text{H}_4\text{Me-4})_3]^{13}$, where lengthening of the Cu–O distances could be expected due to the effect of the extra isocyanide ligand. It is interesting to note that the C1–O2 distances in **4a** and **4b** are comparable to the C=O distance in copper(I)-coordinated acrylaldehyde [1.230(9) Å] in $[\text{CuCl}(\text{C}_3\text{H}_4\text{O})]_n^{14}$. The Cu–O distance [2.296(6) Å], however, in this latter compound is considerably longer than the Cu1–O2 distances found in compounds **4a** and **4b**.

Table II Selected atomic distances (Å) of several relevant copper(I) complexes.

Complex	Cu...Cu benzoato-bridged	Cu–O	C–O	Ref.
$[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)]_2$ 4a	2.638(2)	1.944(5)–2.107(5)	1.249(8)–1.272(10)	a
$[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-2})(\text{NC}_9\text{H}_7)]_2$ 4b	2.667(1)	1.923(5)–2.134(5)	1.240(8)–1.277(8)	a
$[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{PhC}\equiv\text{CPh})_2]_2$	2.779(4) ^b	1.933(10)–1.987(10)	1.232(18)–1.283(20)	12
$[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2(\text{CNC}_6\text{H}_4\text{Me-4})_2]$	2.750(2)	1.969(5)–2.031(6)	1.250(8)–1.262(7)	13
$[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2(\text{CNC}_6\text{H}_4\text{Me-4})_3]$	3.020(3)	1.985(5)–2.078(5) ^c	1.247(10)–1.250(8)	13
$[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)]_4$	2.709(6)–2.770(5)	1.812(13)–1.877(14)	1.23(4)–1.31(4)	17
$[\text{CuCl}(\text{C}_3\text{H}_4\text{O})]_n$		2.296(6)	1.230(9)	14

^a This article. ^b Average of two values which do not differ significantly. ^c Tetracoordinate copper atom.

Solid-state emission

The parallel arrangement of the two quinoline fragments in **4a** and **4b** (see Fig. 3a) has also been found recently by Holt et al. in the structure of $[\text{Cu}_4\text{I}_4(\text{NC}_9\text{H}_7)_4]^{15}$. The broad band emission spectrum of this latter complex at low temperature shows considerable fine structure on the high-energy side due to $\pi \rightarrow \pi^*$ interactions between the closely spaced quinoline units. The low-temperature emission spectra of **4d** (λ excitation at 330 nm; 300–80 K), although they show a broad band due to metal-to-ligand charge transfer (568 nm, 300 K; 554 nm, 80 K) over the entire temperature range studied, do not show fine structure on the high-energy segment. This difference in behaviour is probably due to the only partial overlap between the phenylene moieties of the quinolines in **4d** (see Fig. 3b); in $[\text{Cu}_4\text{I}_4(\text{NC}_9\text{H}_7)_4]^{15}$, there is complete overlap of the quinolines with each other.

Solution structures of **3a** and **4**

Based on the X-ray results for **4a** and **4b** and the similarity of their spectroscopic data, we conclude that in solution compounds **4b-d** preserve the central dinuclear copper(I) unit. However, as suggested by the molecular weight determination of **4d**, some quinoline dissociation may occur from the dimeric $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)]_2$ unit.

The degree of association of the 1:2 copper(I) benzoate/quinoline complex, **3a**, either in the solid state or in solution, is a question that cannot be readily answered. The stoichiometry found is consistent with both a monomeric structure, *i.e.* $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]$, in which the carboxylate group is bidentate bonded to Cu(I), and a dimeric structure, *i.e.* $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$ containing two bridge-bonded benzoate ligands. In both structures (see Fig. 4), coordination of two quinoline ligands to copper completes four-coordination of the metal centre. Of these possible structures, we favour the latter option and believe that **3a**, like compounds **4**, has a structure based on a dimeric copper(I) benzoate unit both in the solid state and in solution.

With this dimeric description, the low molecular weight found for **3** in solution (consistent with a monomeric formulation) can be explained by the almost complete dissociation of one quinoline ligand per dinuclear unit. The resulting species $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2(\text{NC}_9\text{H}_7)_3]$, having a 2:3

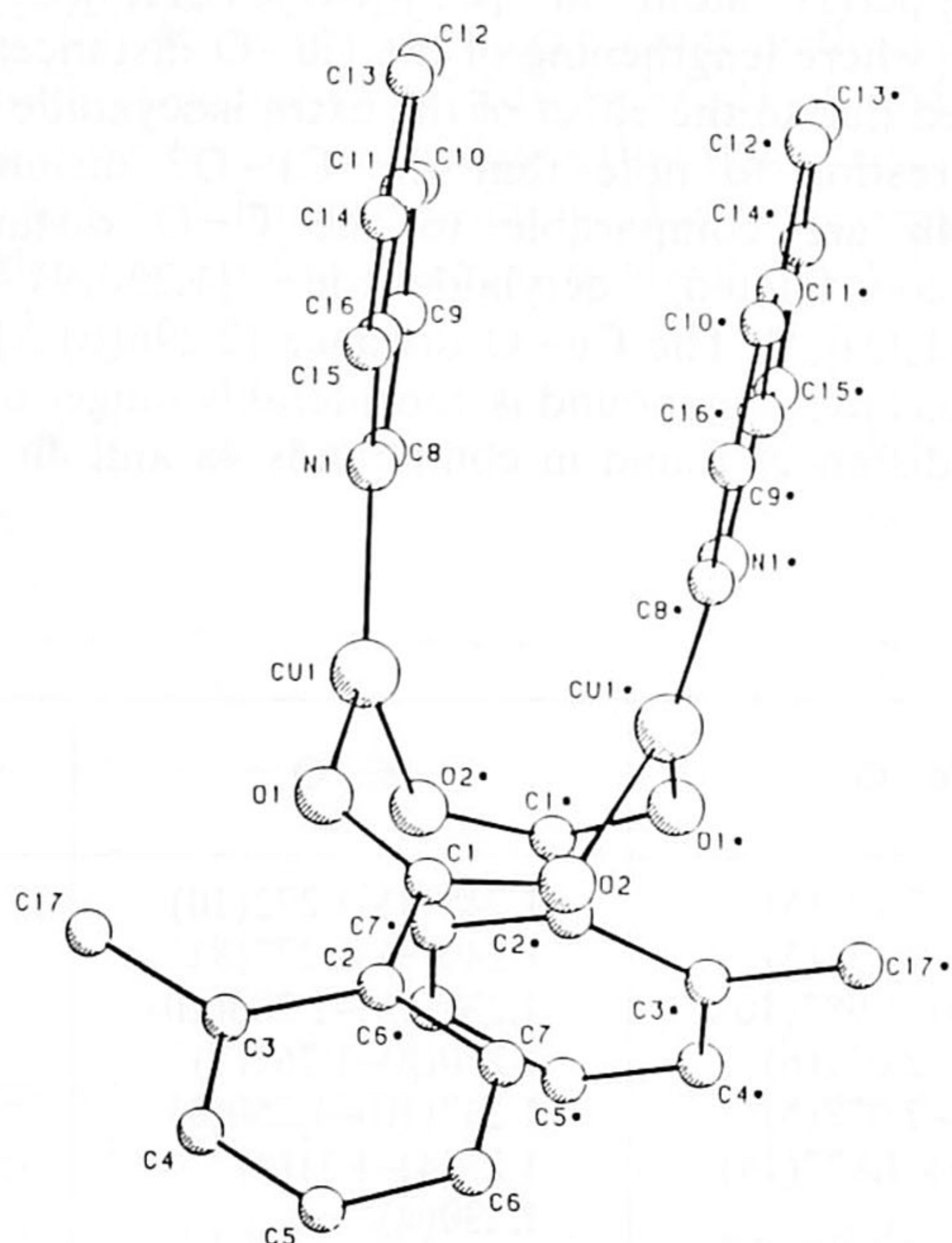


Fig. 3a. PLUTO drawing of **4b** showing the parallel arrangement of the two quinoline ligands.

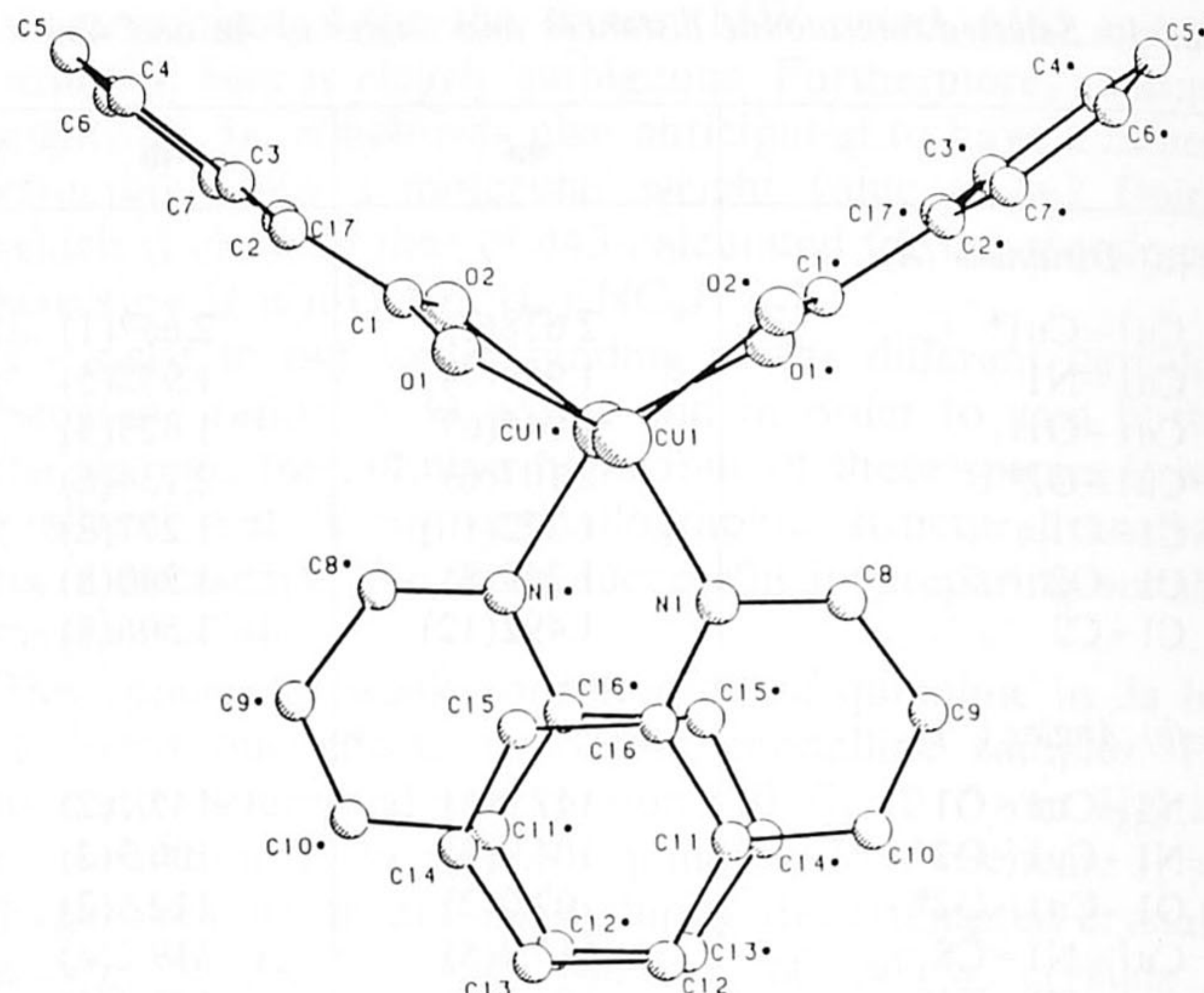


Fig. 3b. PLUTO drawing of **4b** showing the stacked arrangement of the phenylene moieties of the quinoline ligands.

copper(I) benzoate/quinoline ratio, has a precedent in $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2(\text{CNC}_6\text{H}_4\text{Me-}4)_3]^{13}$. The latter structure unambiguously demonstrates that the bonding of more than one ligand per copper(I) atom (in addition to the two benzoate units) does not necessarily cause the breakdown of the dimeric copper(I) benzoate into monomeric units.

Factors determining the formation of 1:1 or 1:2 copper(I) benzoate-quinoline complexes

It was unexpected to find that, whereas Me-substituted benzoates gave rise to the 1:1 complexes $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)]_2$ ($x = 2$, **4b**; $x = 3$, **4c**; $x = 4$, **4d**), the 1:2 complex $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$ (**3a**) was formed with non-substituted benzoate. The difference in stoichiometry between the non-substituted and the *o*-methyl substituted copper(I) benzoate can most likely be explained by steric factors, the bonding of a second equivalent of quinoline to the dimeric copper(I) unit in **4b** being hindered by the *o*-methyl substituent of the benzoate. The importance of steric factors in influencing the course of copper(I) benzoate reactions is also reflected by the fact that bulky 8-methylquinoline does not react with copper(I) benzoates. It is not possible to explain the differences in stoichiometry between **3** and **4** on electronic grounds; the $\text{p}K_a$ of benzoic acid (4.19) and the methyl-substituted benzoic acids (3-Me, 4.27; 4-Me 4.36) are very similar.

Comparison of the decarboxylation reactions of $[\text{Cu}(\mu\text{-O}_2\text{C-C}_6\text{H}_5)(\text{NC}_9\text{H}_7)_2]_2$ (**3a**) and $[\text{Cu}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{Me-}x)(\text{NC}_9\text{H}_7)_2]_2$ ($x = 2$, **4b**; $x = 3$, **4c**; $x = 4$, **4d**)

The decarboxylation of the copper(I) benzoate quinoline compounds **3a** and **4** has been investigated at elevated temperatures in non-coordinating solvents. The choice of non-

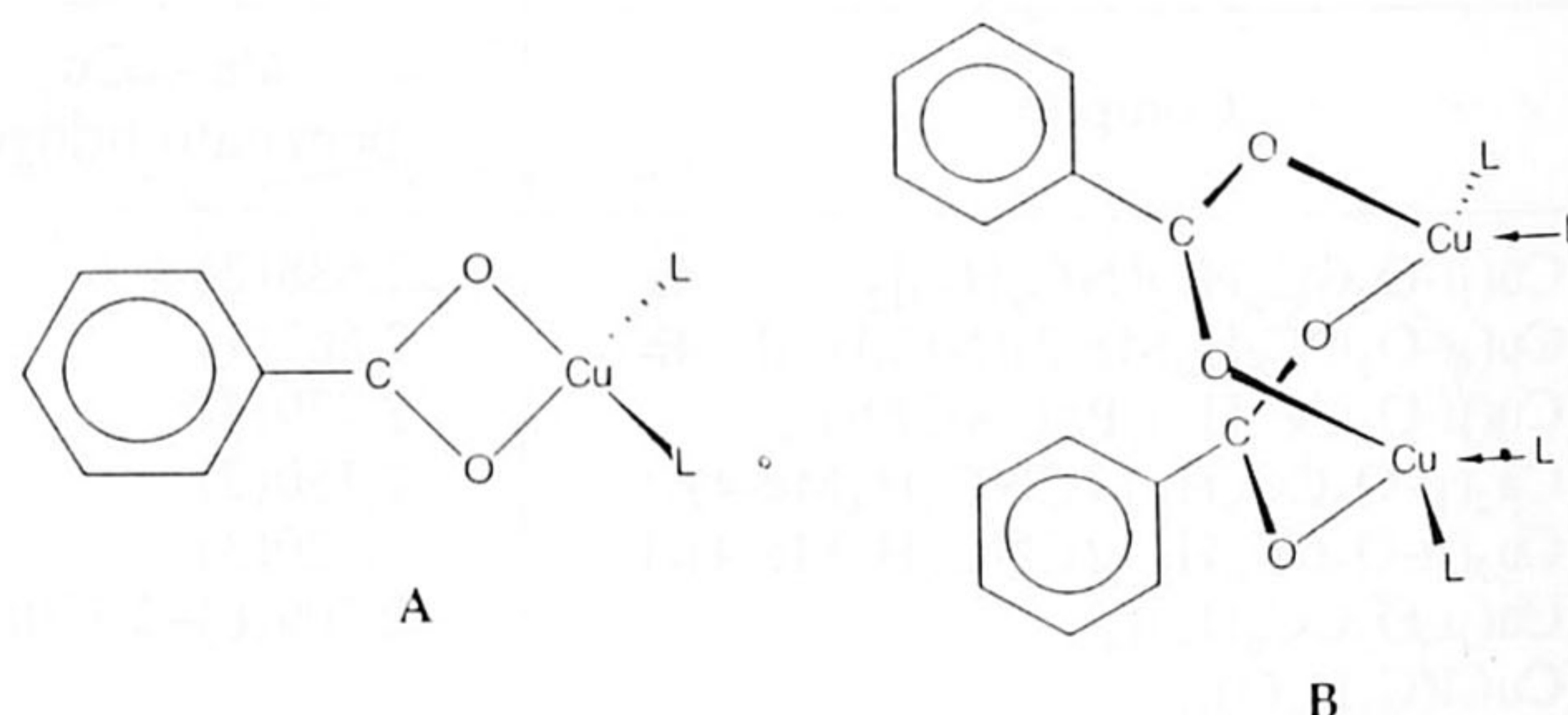


Fig. 4. Possible monomeric (A) and dimeric (B) structures of **3a** in solution and in the solid state.

coordinating solvent was based on the expectation that complexes **3a** and **4**, containing coordinated quinoline, would show the same reactivity as the unactivated copper(I) benzoates in quinoline studied by Cohen⁴. The decarboxylation reaction of **3a** and **4**, when attempted in either refluxing toluene at 110°C or in refluxing decalin at 190°C, was unsuccessful. In the latter case, this result may be primarily due to the insolubility of **3a** and **4** in decalin.

When naphthalene at 218°C was used as the decarboxylation solvent for the 1:2 complex **3a**, it was found that 63% decarboxylation occurred in the orange-red suspension. In Table III, the product distribution of this decarboxylation reaction is given; the experimental procedure, the work-up procedure (which gave a neutral and a basic fraction) and the identification of these products are described in the experimental section.

When the same procedure was carried out with the 1:1 complexes **4**, no decarboxylation was observed. However, addition of 1.1 extra equivalents of quinoline per copper(I) atom to the reaction mixture led to decarboxylation (60% decarboxylation average, see Table III). This indicates that, for the initiation of the decarboxylation reaction, more than one equivalent of quinoline is needed per copper atom. The product distribution of the decarboxylation reactions of complexes **4** are approximately the same as found for **3a** (see Table III). Quinoline and quinoline-containing molecules are, in all cases, the only products identified from the basic fractions.

Table III Product yields (%) in the decarboxylation reactions of the dimeric copper(I) benzoate quinoline complexes **3a** and **4b-d** in naphthalene^a.

Compound	CO ₂	QH	RCOQ	NQ-A	NQ-B	NQ-C	Q ₂ O
3a	63.2	97.6	0.1	1.0	^b	0.1	1.2
4b^c	66.3	99.2	0.1	0.7	^b	^b	^d
4c^c	59.1	99.3	^b	0.7	^b	^b	^b
4d^c	55.8	98.2	0.1	1.7	^b	^b	^d

^a Carbon dioxide and basic fraction only (see experimental). Yields based on an almost quantitative isolation (>90%) of the quinoline fragments; R = aryl ring attached to the carboxylate unit in the starting compound; QH = quinoline; RCOQ = 2-acylquinoline; NQ-A = 8-naphthylquinoline; NQ-B = 2-naphthylquinoline; NQ-C = isomer C of naphthylquinoline (see experimental); Q₂O = 2,2'-diquinolyl ether. ^b Only observed by GC-MS analysis (yield <0.1%). ^c 1.1 equivalent of quinoline per copper atom added to the reaction mixture. ^d Not observed.

These compounds are (i) 2-acylquinolines, (ii) 2,2'-diquinolyl ether and (iii) three different coupling products between naphthalene and quinoline. Naphthylquinoline A (NQ-A) was recovered from every reaction mixture and was always the major coupling product; naphthylquinoline B (NQ-B) and naphthylquinoline C (NQ-C) were the minor products. Based on their mass spectra, particularly the intensity of the P-1 peaks (see experimental), NQ-A and NQ-B are tentatively assigned as 8-naphthylquinoline and 2-naphthylquinoline, respectively.

An important observation is that only a small percentage of the quinoline is recovered as coupling products. It is therefore assumed that the majority of the arene products (benzene or toluene) originate from reaction of [C₆H₅] or [C₇H₇] with the naphthalene solvent.

For the neutral fraction, unfortunately, because of the naphthalene solvent, it was not possible to isolate and characterize the expected products as benzene and toluene (the products of the simple decarboxylation reaction of respec-

tively **3a** and **4**) and as biaryls and benzophenone derivatives⁴.

These successful decarboxylation reactions in naphthalene of **3a** and **4** are the first and only copper-assisted decarboxylations so far reported to have been carried out in a very weak coordinating solvent. It is therefore worthwhile comparing these results with those of Cohen et al. (using copper benzoate and quinoline as solvent). Firstly, the percentage of carbon dioxide recovered (ca. 60%) is comparable to that found for pure copper(I) benzoate in quinoline (65.8% carbon dioxide recovered)⁴. Secondly, the distribution of quinoline and quinoline-containing products is interesting. With **3a** and **4**, quinoline was the major product in all cases and the total of quinoline-containing coupling products does not exceed 2.5%. This low amount of coupling products constitutes a distinct difference between our reaction system and the decarboxylation reaction of copper(I) benzoate in quinoline which produced 17% biquinoline and 2,2'-diquinolyl ether⁴.

The formation of naphthylquinone derivatives in our reactions can only be due to a reaction of quinolylcopper(I), formed *in situ*, or quinolyl radical with naphthalene, whereas the only coupling products of the benzoate fragments with quinoline, the 2-acylquinolines, must originate from an acyl fragment, generated *in situ*; this is discussed in detail in the section dealing with the reaction mechanism. The biquinolyl products and the 2-acylquinolines found by Cohen et al. are most likely formed in a similar manner.

The reaction mechanism

Based on this study of the reactivity of the copper(I) benzoate quinoline complexes **3a** and **4** at elevated temperatures, together with our knowledge of their structures in the solid state and solution, we are now able to propose a detailed reaction mechanism of the copper-assisted decarboxylation reaction.

The most important aspect of this mechanism is that it takes place on a dinuclear copper(I) species. The reaction sequence we propose, is illustrated in Scheme 4 and involves the following steps starting from the dinuclear copper(I) benzoate **I**. In step *i*, one of the longer, and probably weaker, Cu-O bonds of **I** is broken. In the solid state structures of **4a** and **4b**, the different Cu-O bond lengths suggest that the two carboxylate oxygens are not equally strongly bonded to the copper(I) atom. The breaking of one of these Cu-O bonds to afford intermediate **II** is most likely aided by coordination of a second quinoline ligand; in reactions of the 1:1 copper(I) benzoate/quinoline complexes **4**, the addition of extra quinoline was necessary in order to initiate the decarboxylation reaction. In step *ii*, rotation around the C-O and the C-Ar bonds of the now monodentate-bonded benzoate unit in **II** brings the aromatic ring of this benzoate unit close to a copper atom. It is now possible to have an interaction of the copper(I) ion with the π -system between the C_{ipso} and C_{ortho} atoms, as shown in intermediate **III**. From key intermediate **III**, product formation can be achieved via three different reaction routes (A-C). Route **A** involves initial oxidative-addition. In this route, the copper atom moves first across the aromatic ring towards the more electrophilic C_{ipso} atom and inserts into the C_{ipso}-C_{carboxylate} bond to afford the Cu(I)-Cu(III) species **IV**, containing a CO₂⁻ group σ -bonded to a Cu(III) atom.

In route **B**, there is first an initial oxidative-addition combined with an intramolecular Cu-to-Cu electron transfer; the formation of the mixed valence Cu(I)-Cu(III) intermediate **IV** is precluded by donation of one electron from Cu(I) to Cu(III), thereby generating a dinuclear

Cu(II)–Cu(II) intermediate (V) which should be energetically favourable. The interesting consequence of this reaction path, which we favour over route A, is that the Cu(I) d^{10} pair actually acts as an electron reservoir.

Route C involves single-electron transfer (SET) steps; in this case, an electron transfer from the copper(I) atom to the π^* system of the benzoate unit in intermediate III generates an arylcarboxylate radical (VI). This electron "shifts" to the σ^* C_{ipso} – $C_{carboxylate}$ orbital (an analogue π^* – σ^* electron density shift is proposed for the dissociation of a halide ion from aryl halides in the $S_{RN}1$ reaction¹⁶) and the C_{ipso} – $C_{carboxylate}$ bond can be broken.

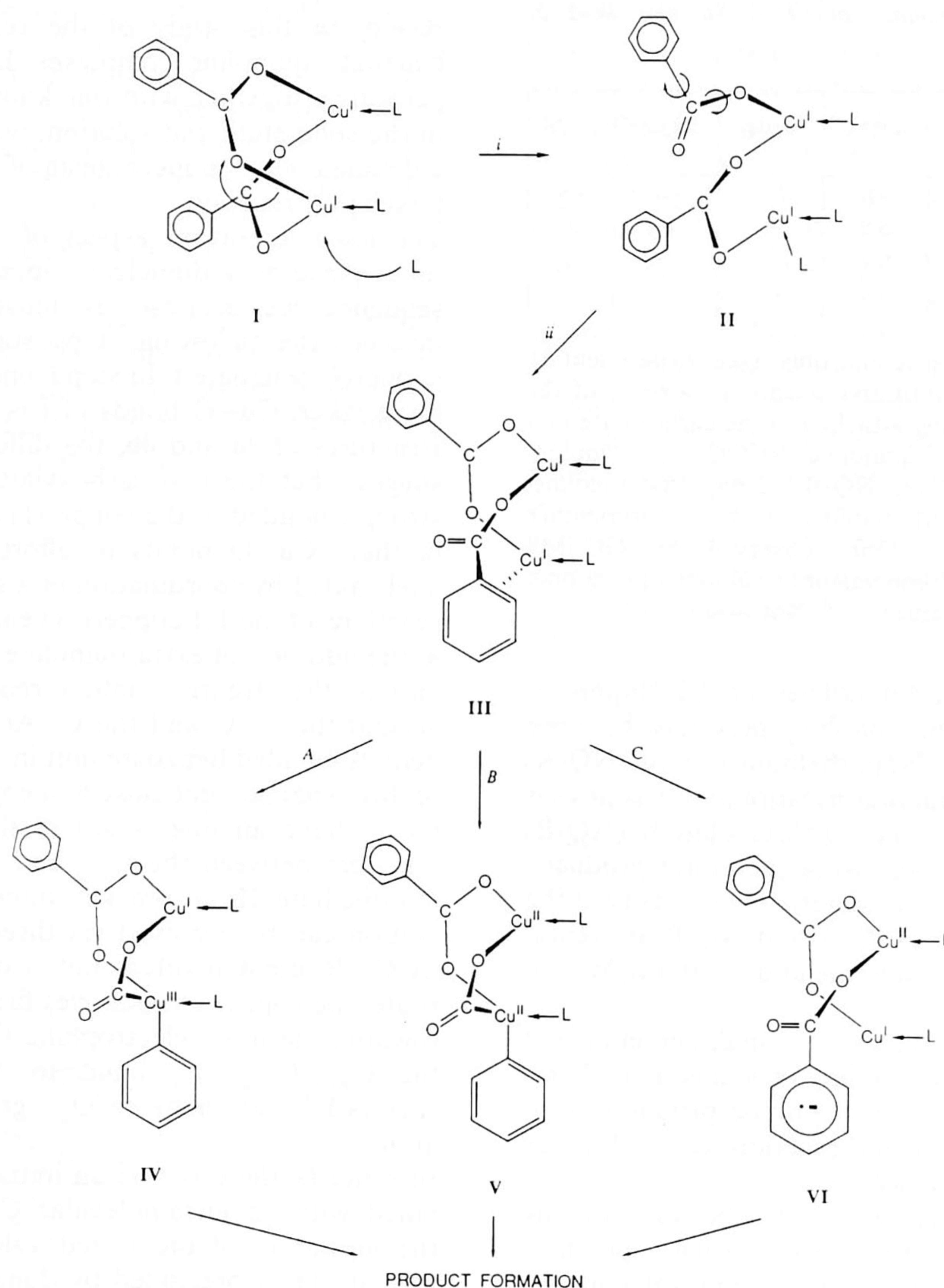
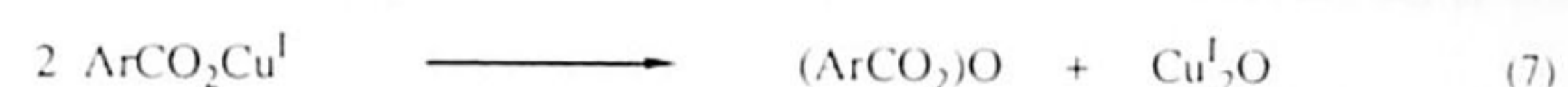
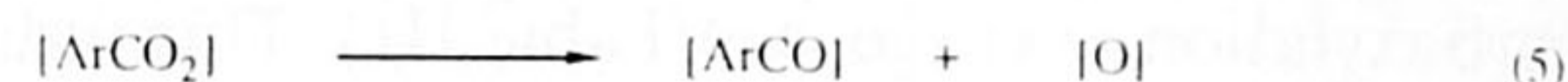
Product formation can now be anticipated from the proposed intermediates IV, V and VI. Attack of either a solvent molecule or a coordinated quinoline ligand on the arylcopper intermediate IV or V would yield arene (benzene or toluene) and naphthylcopper or quinolylcopper derivatives, respectively (Eqn. 3). Alternatively, an arene could also be formed if the arylcarboxylate radical intermediate VI splits off an aryl radical and carbon dioxide in one step. An aryl radical so generated could then react further with solvent or quinoline affording arene and naphthyl or quinoline radicals (Eqn. 4). A secondary reaction of the quinolyl- and/or naphthyl-copper species or radicals generated in this process can then be used to explain the formation of organic naphthylquinolyl derivatives.

The acylquinolines generated in the copper-quinoline decarboxylation reaction can only be formed when a carbon-oxygen bond of the carboxylate unit is broken. This

could occur via either insertion of a copper atom into a carbon-oxygen bond or by an electron transfer reaction from copper(I) intermediate III to the carboxylate fragment, initiating C–O rather than C–C bond breakage (Eqn. 5). Further reaction of the oxygen atom released during this reaction would then account for the formation of 2,2'-diquinolyl ether (Eqn. 6). Cohen assigned the formation of the acylquinolines to a reaction of the acid anhydride (used as a starting compound) with quinolylcopper(I)



R = quinolyl, naphthyl



Scheme 4. Possible monomeric (A) and dimeric (B) structures of **3a** in solution and in the solid state.

formed *in situ*. In our reactions, however, no acid anhydride is originally present, though its *in situ* formation by "dissociation" of copper(I) oxide from a dinuclear copper(I) benzoate unit cannot be totally excluded (Eqn. 7).

Concluding remarks

Based on this study of the reactivity and structure of dimeric 1:1 and 1:2 copper(I) benzoate/quinoline complexes, we have developed an improved mechanism for the copper-assisted decarboxylation reaction of benzoic acids in quinoline. This proposed mechanism, based on a dinuclear copper(I) unit as the reactive entity, has the advantage that the formation of trivalent organocopper intermediates can be circumvented, since the dinuclear Cu(I) d^{10} pair can act as a potential electron reservoir. Moreover, the second copper atom which is held close to the first by the carboxylato bridge can assist the insertion process of the latter copper atom by providing the second electron required for the breaking of the C1–C2 bond and the formation of the two Cu–C bonds; this generates two copper(II) atoms instead of a copper(I) and a copper(III) atom. A definite choice, however, between this route **B** and the single electron transfer route **C** cannot be made. Furthermore, our study revealed that the nature of coordinating ligands and/or solvents is extremely important in determining the course of copper-catalysed and -assisted reactions.

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Supplementary material

Data concerning the X-ray structure determinations can be obtained from the authors.

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