Notes

Oxidative Addition of Dibenzoyl Peroxide on Metallic Copper. The Crystal Structure of $[\{Cu(C_6H_5CO_2)_2(py)\}_2]$†

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Dibenzoyl peroxide in pyridine (py) undergoes facile oxidative addition with metallic copper and affords the complex $[\{Cu(C_6H_5CO_2)_2(py)\}_2]$. Crystals are monoclinic, space group $P2_1/n$, with cell parameters $a = 10.036(1)$, $b = 10.467(1)$, $c = 17.344(2)$ Å, $\beta = 98.66(1)°$, and $Z = 2$. The copper atoms are bridged in pairs by four benzoate groups to form binuclear molecules. The copper atom is 0.217 Å out of the plane of the four oxygen atoms (Cu–O from 1.960 to 1.979 Å) to which it is bonded, towards the nitrogen atom of the pyridine ligand. The octahedral co-ordination around the copper atom is completed by the nitrogen atom of the pyridine molecule (Cu–N 2.170 Å) and by the second copper atom (Cu ··· Cu 2.658 Å). The binuclear molecule as a whole possesses a centre of symmetry.

Oxidative-addition reactions are very important in transition metal chemistry.[1] They are widespread and in many cases key steps in the activation of σ bonds in a great number of catalytic processes. While copper complexes are widely used as catalysts in the decomposition of disubstituted peroxides[2] only one early preliminary report deals with the reaction of metallic copper and diacyl peroxides.[3] Since no well defined copper(0) complexes are known from the literature[4] our aim was to investigate the oxidative-addition reaction of the O–O bond in dibenzoyl peroxide on metallic copper.

Experimental

Reactions were carried out under argon. Infrared spectra were recorded on a Specord 75IR (Carl Zeiss, Jena) spectrometer and the magnetic susceptibility determined on a Bruker B-E 10B8 system.

Preparation of Tetrakis(benzoato)bis(pyridine)dicopper(II).—A mixture of dibenzoyl peroxide (484 mg, 2 mmol), copper powder (127 mg, 2 mmol), and pyridine (5 cm^3) was stirred under argon for 1.5 h. The dark green solution was filtered, diethyl ether (20 cm^3) added, and left overnight to yield nice blue crystals. They were filtered off, washed with ether, and dried *in vacuo* to give crystals of $[\{Cu(C_6H_5CO_2)_2(py)\}_2]$ (60 mg, 78%), m.p. 305—308 °C (Found: C, 59.2; H, 4.0; N, 3.6. $C_{38}H_{30}Cu_2N_2O_8$ requires C, 59.3; H, 3.9; N, 3.6%); $\nu(CO_2)$ 1 607 and 1 483 cm^{-1}.

Crystallography.—Crystals suitable for *X*-ray diffraction were obtained by recrystallization from dichloromethane–ether.

Crystal data. $C_{38}H_{30}Cu_2N_2O_8$, $M = 769.75$, monoclinic, $a = 10.036(1)$, $b = 10.467(1)$, $c = 17.344(2)$ Å, $\beta = 98.66(1)°$, $U = 1\,801.0(6)$ Å^3, space group $P2_1/n$ (alternative $P2_1/c$, No. 14), $Z = 2$, $D_c = 1.42$ g cm^{-3}, $F(000) = 788$, $\mu(\text{Cu-K}_\alpha) = 18.6$ cm^{-1}, $\lambda = 1.541\,84$ Å.

Measurements.—A bluish-green crystal *ca.* 0.09 × 0.12 × 0.25 mm was mounted on an Enraf-Nonius CAD4 diffractometer and exposed to graphite-monochromated Cu-K_α radiation. The unit-cell dimensions were determined by least squares treatment of diffractometer angles for 25 automatically centred reflections in the range $28 \leqslant \theta \leqslant 31°$. Intensity data were collected in the ω—2θ mode with a scan width = $0.3 + 0.3 \tan\theta$, ω scan speed 1.0—20.0° min^{-1}. 3 891 Reflections were measured ($1.5 \leqslant \theta \leqslant 75°$, $\pm h, k, l$) of which 3 261 were unique and corrected for Lorentz, polarization, and absorption[5] effects (maximum, minimum transmission factors = 1.597 and 0.651). Only 2 757 structure amplitudes with $I \geqslant 3.0\sigma(I)$ were used in further analysis. Three standard reflections were measured every hour, but no intensity variation was detected.

Structure solution and refinement. The structure was solved by direct methods (MULTAN 82).[6] Full-matrix least squares minimized the $w(\Delta F)^2$ function with all non-hydrogen atoms anisotropic. The weighting scheme was $w = 4F_o^2/\sigma^2(F_o^2)$. Hydrogen atoms were introduced in calculated positions with fixed isotropic thermal parameters $B_{iH} = B_{iX} + 1$ in Å^2, where X is either the nitrogen or the *ipso* carbon atom of the aromatic rings, N(10), C(4), and C(4′) respectively. They were not refined, however. Refinement of 226 structural parameters converged at $R = 0.045$ and $R' = 0.064$. The final atomic co-ordinates are listed in Table 1.

All calculations were performed on a PDP11/34 minicomputer, programs and sources of scattering factor data are given in ref. 7.

Additional material available from The Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Dibenzoyl peroxide in pyridine reacts rapidly with copper powder at room temperature giving a dark green solution. The

$$2Cu^0 + 2(C_6H_5CO_2)_2 + 2(py) \longrightarrow [\{Cu(C_6H_5CO_2)_2(py)\}_2] \quad (1)$$

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† Tetrakis(benzoato)bis(pyridine)dicopper(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates for non-hydrogen atoms, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.595 81(4)	0.049 92(3)	0.552 63(2)
O(1)	0.675 5(2)	−0.121 6(2)	0.548 6(1)
O(2)	0.515 9(2)	−0.206 1(1)	0.460 1(1)
C(3)	0.624 3(2)	−0.211 9(2)	0.506 6(1)
C(4)	0.698 1(3)	−0.335 8(3)	0.513 0(1)
C(5)	0.821 3(4)	−0.346 2(3)	0.558 9(2)
C(6)	0.885 7(5)	−0.465 6(4)	0.568 2(3)
C(7)	0.827 8(5)	−0.568 8(3)	0.532 0(2)
C(8)	0.704 9(4)	−0.558 7(3)	0.485 1(2)
C(9)	0.641 2(3)	−0.444 5(3)	0.475 2(2)
O(1′)	0.680 2(2)	0.099 4(2)	0.462 2(1)
O(2′)	0.522 0(2)	0.013 9(2)	0.374 0(1)
C(3′)	0.629 0(3)	0.073 1(2)	0.393 5(1)
C(4′)	0.701 3(3)	0.121 2(2)	0.328 7(1)
C(5′)	0.817 4(3)	0.193 0(3)	0.345 0(1)
C(6′)	0.877 8(3)	0.241 5(4)	0.285 4(2)
C(7′)	0.823 2(4)	0.219 7(3)	0.209 1(1)
C(8′)	0.709 5(4)	0.146 1(4)	0.192 3(1)
C(9′)	0.649 0(3)	0.0963 (3)	0.252 4(1)
N(10)	0.750 4(2)	0.116 7(2)	0.645 0(1)
C(11)	0.864 5(5)	0.058 6(4)	0.663 5(3)
C(12)	0.954 8(5)	0.083 5(5)	0.729 7(4)
C(13)	0.918 0(6)	0.176 1(5)	0.778 5(2)
C(14)	0.803 6(5)	0.243 3(6)	0.758 9(2)
C(15)	0.724 4(4)	0.209 3(4)	0.693 3(2)

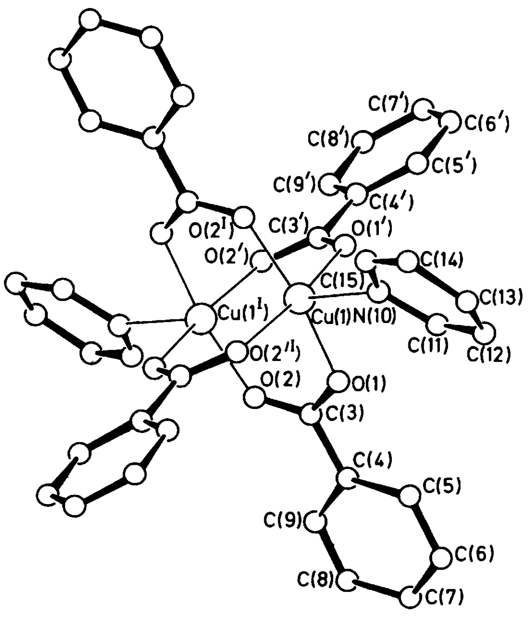

Figure. Perspective view of the molecular structure of [{Cu($C_6H_5CO_2$)$_2$(py)}$_2$] showing the atom-labelling scheme

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Cu(1)–Cu(1^{I})	2.658(1)	O(1)–C(3)	1.256(3)
Cu(1)–O(1)	1.971(2)	O(2)–C(3)	1.254(3)
Cu(1)–O(2^{I})	1.976(2)	C(3)–C(4)	1.489(4)
Cu(1)–O(1′)	1.960(2)	O(1′)–C(3′)	1.256(3)
Cu(1)–O($2'^{I}$)	1.979(2)	O(2′)–C(3′)	1.242(3)
Cu(1)–N(10)	2.170(3)	C(3′)–C(4′)	1.513(4)
Cu(1^{I})–Cu(1)–O(1)	82.7(1)	O(2^{I})–Cu(1)–N(10)	98.4(1)
Cu(1^{I})–Cu(1)–O(2^{I})	84.8(1)	O(1′)–Cu(1)–O($2'^{I}$)	167.2(1)
Cu(1^{I})–Cu(1)–O(1′)	84.8(1)	O(1′)–Cu(1)–N(10)	99.1(2)
Cu(1^{I})–Cu(1)–O($2'^{I}$)	82.5(1)	O($2'^{I}$)–Cu(1)–N(10)	93.7(1)
Cu(1^{I})–Cu(1)–N(10)	174.9(1)	Cu(1)–O(1)–C(3)	125.0(3)
O(1)–Cu(1)–O(2^{I})	167.5(1)	Cu(1^{I})–O(2)–C(3)	122.3(3)
O(1)–Cu(1)–O(1′)	89.2(2)	O(1)–C(3)–O(2)	125.2(4)
O(1)–Cu(1)–O($2'^{I}$)	90.0(2)	O(1)–C(3)–C(4)	117.1(4)
O(1)–Cu(1)–N(10)	94.1(2)	O(2)–C(3)–C(4)	117.6(4)
O(2^{I})–Cu(1)–O(1′)	89.9(1)	Cu(1)–O(1′)–C(3′)	122.5(3)
O(2^{I})–Cu(1)–O($2'^{I}$)	88.1(1)	Cu(1^{I})–O(2′)–C(3′)	124.6(3)
		O(1′)–C(3′)–O(2′)	125.6(5)
		O(1′)–C(3′)–C(4′)	117.3(4)
		O(2′)–C(3′)–C(4′)	117.1(4)

[I] Indicates centrosymmetrically related positions.

copper dissolves totally and on addition of ether blue crystals of [{Cu($C_6H_5CO_2$)$_2$(py)}$_2$] are deposited in good yield. The mechanism of reaction (1) is probably stepwise as the benzoyl radical reacts with Cu^0 to give copper(I) benzoate, which then in a subsequent reaction with a further benzoyl radical results in the binuclear copper(II) carboxylate complex. These processes may be regarded as successive oxidative additions of Cu^0 ending with the copper(II) carboxylate compound. Under identical conditions, bis(triphenylmethyl) peroxide and di-t-butyl peroxide did not react with metallic copper. The complex [{Cu($C_6H_5CO_2$)$_2$(py)}$_2$] is paramagnetic at room temperature ($\mu_{\text{eff.}}$ = 2.34) showing antiferromagnetic interaction, which is usually found for this type of binuclear copper(II) compound.[8]

Description of the Crystal Structure.—A molecular diagram of the title compound [{Cu($C_6H_5CO_2$)$_2$(py)}$_2$] with the atom numbering is depicted in the Figure; relevant bond distances and angles are given in Table 2.

The complex has the expected dimeric form with two copper(II) atoms surrounded by four benzoate groups and two pyridine ligands. This binuclear molecule possesses a centre of symmetry. The nearest neighbours of the copper atom are the four oxygen atoms of the bridging benzoate ligands in a square planar arrangement. The Cu–O distances are identical [from 1.960(2) to 1.979(2) Å] within experimental error. A square-based pyramidal arrangement about the copper atom is completed by the nitrogen of the pyridine ligand at 2.170(3) Å from the copper atom. The copper atom lies 0.217(1) Å out of the least-squares plane defined by the four oxygen atoms, towards the nitrogen atom. The octahedral environment about the copper atom is completed by the other copper atom of the dimer. The Cu–Cu distance is 2.658(1) Å, and the angle formed by the line of Cu(1^{I}),Cu(1),N(10) atoms (within 0.07 Å of the line) and the normal of the plane of four oxygen atoms to which Cu(1) is bonded (within 0.002 Å of the plane) is near zero [0.17(7)°]. Bond distances and angles in the co-ordination sphere fall within the range found in [{Cu(CH_3CO_2)$_2$(py)}$_2$],[9,10] [{Cu($ClCH_2CO_2$)$_2$(2Me-py)}$_2$],[11] and [Cu_2(CH_3CO_2)$_4$(pyrazine)].[12] The geometries of the phenyl and pyridine rings are normal.

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