A NOVEL SYNTHETIC METHOD FOR AND THE STRUCTURE OF TETRAKIS(μ-BENZOATO-O:O')-BIS(TRIPHENYLPHOSPHINE OXIDE)DICOPPER(II). OXIDATIVE ADDITION OF DIBENZOYLPEROXIDE TO METALLIC COPPER

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PLEASE SCROLL DOWN FOR ARTICLE

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Dibenzoyl peroxide undergoes oxidative addition to metallic copper with triphenylphosphine in a mixed solvent (acetone, dichloromethane and trichloromethane) and affords the binuclear complex $[Cu(C_6H_5COO)_2(Ph_3PO)]_2$. Crystals are monoclinic, space group $A2/a$, with cell parameters, $a = 24.337(3)$, $b = 10.566(1)$, $c = 21.579(2)$ Å, $\beta = 93.18(1)°$, $V = 5540(1)$ Å^3, $Z = 4$, $R = 0.042$, and $R_w = 0.044$ for 5872 observed reflections. Each copper ion is coordinated by four bridging bidentate benzoate ligands and one triphenylphosphine oxide group to form dimeric binuclear molecules.

Keywords: Copper, binuclear complex, oxidative addition, crystal structure

INTRODUCTION

Oxidative additions are very important in transition metal chemistry and catalytic reactions. They represent key steps in the activation of σ bonds in a great number of catalytic processes.[1] Copper complexes are widely used as catalysts in the decomposition of disubstituted peroxides.[2] Our aim is to investigate oxidative-additions of the O–O bond in dibenzoyl peroxide to metallic copper.

The title complex has been already reported by two groups, and the published method involves reacting copper benzoate and triphenylphosphine oxide.[3,4] Both authors spectroscopically proposed a carboxylate-bridged binuclear structure, which has not yet been confirmed by X-ray analysis.

This report concerns a new oxidative preparation method of the copper complex, and the X-ray structure analysis of the title complex.

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EXPERIMENTAL

Synthesis and analysis

Reactions were carried out under nitrogen. Solvents were purified by usual means. Triphenylphosphine (0.5 mmol, 131 mg) was added to a mixture of dibenzoyl peroxide (1 mmol, 242 mg) and copper powder (0.5 mmol, 31.8 mg) in a mixed solvent of acetone (20 cm^3), dichloromethane (20 cm^3) and trichloromethane (20 cm^3). The solution was stirred for 48 h at room temperature. The dark green solution was filtered, and left to yield blue crystals. They were washed and dried *in vacuo*. Yield: 70%. The crystals are stable in air. Elemental analyses were performed on an ERBA-1106 instrument. Copper was determined on a JA96–970 spectrometer. Found: C, 65.94; H, 4.33; Cu, 10.95%. $C_{64}H_{50}O_{10}P_2Cu_2$ requires: C, 65.80; H, 4.31; Cu, 10.88%. IR spectra were measured in KBr pellets on a JEOL JIR-5300 spectrometer. Electronic spectra were observed with a Hitachi 330 spectrophotometer.

Crystal structure determination

Crystal Data: $C_{64}H_{50}O_{10}P_2Cu_2$, $M_w = 1168.1$, monoclinic, space group $A2/a$, $a = 24.337(3)$, $b = 10.566(1)$, $c = 21.579(2)$ Å, $\beta = 93.18(1)°$, $V = 5540(1)$ Å^3, $Z = 4$, $F(000) = 2408$, $\rho_{obs} = 1.40$, $\rho_{calc} = 1.400$ Mg m^{-3}, μ(Mo Kα) = 0.92 mm^{-1}.

Density was measured by flotation with aqueous K_2HgI_4. A prismatic crystal of approximate dimensions $0.5 \times 0.5 \times 0.35$ mm was mounted on a Rigaku AFC-5 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were determined by least-squares refinement of 20 accurately centred reflections ($25.52 \leqslant 2\theta \leqslant 30.41°$). Intensity measurements: θ–2θ scan technique; scan speed 4° min^{-1} in θ; scan width $(1.0 + 0.35 \tan \theta)°$ in θ; counting time of background 3 s. Three standard reflections, $-_6, 2, 12$, $1-_68$ and $6, 0, 12$, monitored every 100 reflections, showed intensity variation of $< \pm 3\%(F)$. The observed index range was h; $-34/34$, k; 0/15, l; 0/30 ($2\theta \leqslant 60°$); 8689 reflections were collected, 8070 unique, $R_{int} = 0.020$, and 5872 used [$F_o \geqslant 3\sigma(F)$]. Intensities were corrected for Lorentz and polarization effect, but not for absorption. Though systematic absences (*hkl*, $k + l = 2n + 1$; *h0l*, $h = 2n + 1$) suggest two possibilities of space group, Aa and $A2/a$, the latter converged to a structure possessing undistorted geometry.

All the non-H atoms were found using direct methods (MULTAN84).[5] After several cycles of block-diagonal least-squares refinement, positional parameters of H were calculated. In the final cycle, 453 parameters were included, anisotropic thermal parameters for non-H atoms, and a constant isotropic thermal parameter, $B = 4.0$ Å^2, for H atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1$. The number of observations per refined parameter was 12.96 and $S = 1.34$. The final R and R_w values were 0.042, and 0.044, respectively, and the maximum shift/e.s.d. was 0.11. In the final difference map, $\Delta \rho$ excursions, 0.30 and -0.20 eÅ^{-3}, were not significant. Scattering factors were taken from International Tables for X-Ray Crystallography.[6] Computations were performed using a Panafacom U-1200 IIA with the Rigaku RASA-5P program package system and a HITAC M-680H at the Computer Centre of the University of Tokyo with a UNICS program system (local version).[7] Lists of anisotropic thermal parameters, H-atom parameters, and observed and calculated structure factors are available from the authors on request.

RESULTS AND DISCUSSION

Reaction conditions

Dibenzoyl peroxide and triphenylphosphine react with copper powder at room temperature giving a green solution. After a few days, green crystals were deposited in good yield.

$$2Cu + 4(C_6H_5COO)_2 + 2(PPh_3) \rightarrow [Cu(C_6H_5COO)_2(Ph_3PO)]_2 + 2(C_6H_5CO)_2O$$
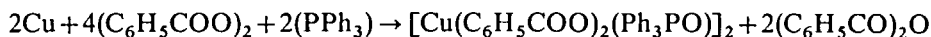
The mechanism of the reaction is probably stepwise as the benzoyl radical reacts with Cu to give copper(I) benzoates which then in a subsequent reaction with a further benzoyl radical result in the binuclear copper(II) carboxylate complex. These processes may be regarded as involving successive oxidations of Cu, ending with the copper(II) carboxylate compound. Triphenylphosphine, which is used as an auxiliary ligand in the system, simultaneously undergoes oxidation by benzoyl peroxide to form triphenylphosphine oxide. In the IR spectra, the P=O stretching frequency, observed at $1189 \, cm^{-1}$, shows a slight shift from free $Ph_3PO(1195 \, cm^{-1})$, pointing to the fact that the coordination of Ph_3PO occurs through oxygen in the complex. Therefore, the use of metallic copper and benzoyl peroxide is characteristic of a novel synthetic method, quite different to that employed in previous preparations of the complex.

The observed absorption band maxima in the electronic spectra, as well as the IR spectra, agreed with those in the literature.[4]
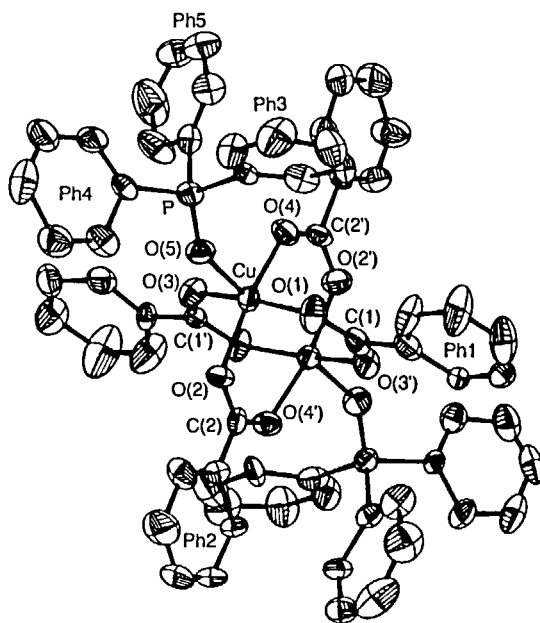

FIGURE 1 Perspective view of the title complex dimer with the atom numbering. Thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

Molecular structure

An asymmetric unit of the cell contains half of the centrosymmetric molecule. The final positional and equivalent thermal parameters of non-H atoms are given in Table I. Figure 1 illustrates the conformation of the molecule by ORTEP,[8] with the atom numbering scheme. In the figure, symbols for phenyl rings, Ph1–Ph5, are used

TABLE I

Fractional coordinates and equivalent isotropic thermal parameters for $[Cu(C_6H_5COO)_2(Ph_3PO)]_2$[a]

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Cu	0.04923(1)	0.20991(3)	0.27128(1)	2.379(6)
P	0.16665(3)	0.13873(7)	0.36154(3)	2.67(2)
O(1)	0.07280(9)	0.3836(2)	0.2522(1)	3.87(6)
O(2)	0.05865(9)	0.1645(2)	0.18416(9)	3.60(5)
O(3)	0.00969(8)	0.0499(2)	0.2852(1)	3.50(5)
O(4)	0.02498(8)	0.2712(2)	0.35101(9)	3.50(5)
O(5)	0.12874(8)	0.1442(2)	0.30467(9)	3.38(5)
C(1)	0.0401(1)	0.4665(3)	0.2297(1)	2.90(6)
C(2)	0.0222(1)	0.1863(3)	0.1418(1)	2.75(6)
C(11)	0.0631(1)	0.5974(3)	0.2220(1)	3.11(7)
C(12)	0.1143(2)	0.6261(4)	0.2480(2)	5.9(1)
C(13)	0.1345(2)	0.7488(4)	0.2467(3)	7.9(2)
C(14)	0.1036(2)	0.8426(3)	0.2177(2)	5.6(1)
C(15)	0.0535(2)	0.8140(3)	0.1902(2)	4.21(9)
C(16)	0.0324(1)	0.6917(3)	0.1922(1)	3.66(8)
C(21)	0.0369(1)	0.1592(3)	0.0767(1)	3.02(7)
C(22)	0.0886(1)	0.1147(4)	0.0644(2)	4.36(9)
C(23)	0.1016(2)	0.0909(5)	0.0039(2)	6.0(1)
C(24)	0.0629(2)	0.1116(5)	−0.0445(2)	5.7(1)
C(25)	0.0115(2)	0.1553(4)	−0.0324(2)	4.7(1)
C(26)	−0.0019(1)	0.1799(3)	0.0282(1)	3.82(8)
C(31)	0.2025(1)	0.2864(3)	0.3765(1)	3.02(6)
C(32)	0.1718(1)	0.3969(3)	0.3770(2)	4.00(8)
C(33)	0.1989(2)	0.5122(3)	0.3867(2)	5.1(1)
C(34)	0.2548(2)	0.5155(4)	0.3964(2)	5.7(1)
C(35)	0.2852(2)	0.4068(4)	0.3959(3)	6.7(1)
C(36)	0.2588(1)	0.2911(4)	0.3854(2)	5.0(1)
C(41)	0.2190(1)	0.0203(3)	0.3535(1)	2.97(6)
C(42)	0.2444(2)	−0.0407(3)	0.4046(2)	4.32(9)
C(43)	0.2872(2)	−0.1249(4)	0.3966(2)	5.5(1)
C(44)	0.3045(2)	−0.1498(4)	0.3382(2)	5.4(1)
C(45)	0.2789(2)	−0.0921(4)	0.2875(2)	5.4(1)
C(46)	0.2364(1)	−0.0065(4)	0.2947(2)	4.15(9)
C(51)	0.1330(1)	0.1007(3)	0.4313(1)	3.10(7)
C(52)	0.1451(1)	0.1592(4)	0.4877(2)	4.21(9)
C(53)	0.1187(2)	0.1215(5)	0.5401(2)	5.1(1)
C(54)	0.0812(2)	0.0265(5)	0.5368(2)	5.7(1)
C(55)	0.0683(2)	−0.0307(4)	0.4805(2)	6.9(2)
C(56)	0.0934(2)	0.0057(4)	0.4273(2)	5.1(1)

[a] Estimated standard deviations are in parentheses. The isotropic thermal parameter is defined as: $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$.

for simplicity; Ph1 denotes C(11)–C(16), Ph2 C(21)–C(26), and so on. Selected bond distances and angles are listed in Tables II and III.

The Cu atom is coordinated by five O atoms: four of them, O(1)–O(4), belong to bridging carboxyl groups, and O(5) to the Ph_3PO group. The bond distances between Cu and the four carboxyl O's, are in the range 1.959(2)–1.976(2) Å (av. 1.968 Å), and similar values have been observed in *tetrakis*(acetato)bis(triphenylphosphine)-dicopper(II) (av. 1.956(5) Å).[9] The fifth O(5) atom in the Ph_3PO group gives a significantly longer distance from Cu, 2.143 Å, than the other four O's. The five O atoms form a distorted square pyramid with O(5) at the apical position. The basal plane forms an almost perfect square, with 2.750(3)–2.815(3) Å (av. 2.768 Å) lengths, and the Cu atom lies 0.210 Å above it. The four C–O distances in the two carboxyl bridges are not significantly different (av. 1.255 Å), and possess comparable values to those in other acetate-bridging dicopper complex.[9]

There have been many structural reports concerning bridged binuclear copper(II) compounds,[9–12] similar to the present complex. Some authors have been interested

TABLE II
Selected bond distances (Å) for $[Cu(C_6H_5COO)_2(Ph_3PO)]_2$.

Bond	Length	Bond	Length
Coordinated moiety			
Cu–O(1)	1.973(2)	Cu–O(4)	1.959(2)
Cu–O(2)	1.965(2)	Cu–O(5)	2.143(2)
Cu–O(3)	1.976(2)		
Bridging benzoate group			
O(1)–C(1)	1.262(4)	O(2)–C(2)	1.260(4)
O(3)–C(1')	1.248(4)	O(4)–C(2')	1.251(4)
C(1)–C(11)	1.505(4)	C(2)–C(21)	1.496(4)
C(11)–C(12)	1.372(6)	C(21)–C(22)	1.383(5)
C(11)–C(16)	1.382(5)	C(21)–C(26)	1.387(4)
C(12)–C(13)	1.387(8)	C(22)–C(23)	1.383(6)
C(13)–C(14)	1.374(8)	C(23)–C(24)	1.384(7)
C(14)–C(15)	1.360(6)	C(24)–C(25)	1.372(6)
C(15)–C(16)	1.392(5)	C(25)–C(26)	1.390(5)
Triphenylphosphine oxide group			
P–O(5)	1.494(2)	C(42)–C(43)	1.388(6)
P–C(31)	1.808(3)	C(43)–C(44)	1.377(6)
C(31)–C(32)	1.387(5)	C(44)–C(45)	1.369(6)
C(31)–C(36)	1.374(5)	C(45)–C(46)	1.390(6)
C(32)–C(33)	1.396(5)	P–C(51)	1.799(3)
C(33)–C(34)	1.365(6)	C(51)–C(52)	1.383(5)
C(34)–C(35)	1.367(7)	C(51)–C(56)	1.390(5)
C(35)–C(36)	1.394(7)	C(52)–C(53)	1.389(6)
P–C(41)	1.801(3)	C(53)–C(54)	1.356(7)
C(41)–C(42)	1.392(5)	C(54)–C(55)	1.377(7)
C(41)–C(46)	1.389(5)	C(55)–C(56)	1.384(7)

TABLE III

Selected bond angles (°) for $[Cu(C_6H_5COO)_2(Ph_3PO)]_2$.

Atoms	Angle	Atoms	Angle
Coordinated moiety			
O(1)–Cu–O(2)	88.7(1)	O(2)–Cu–O(4)	167.7(1)
O(1)–Cu–O(3)	167.7(1)	O(2)–Cu–O(5)	95.25(9)
O(1)–Cu–O(4)	88.9(1)	O(3)–Cu–O(4)	88.65(9)
O(1)–Cu–O(5)	95.97(9)	O(3)–Cu–O(5)	96.31(9)
O(2)–Cu–O(3)	91.15(9)	O(4)–Cu–O(5)	97.01(9)
Bridging benzoate group			
Cu–O(1)–C(1)	122.8(2)	Cu–O(2)–C(2)	122.4(2)
O(1)–C(1)–O(3')	125.8(3)	O(2)–C(2)–O(4')	126.1(3)
Cu–O(3)–C(1')	123.6(2)	Cu–O(4)–C(2')	123.4(2)
O(1)–C(1)–C(11)	116.7(3)	O(2)–C(2)–C(21)	116.8(3)
O(3')–C(1)–C(11)	117.4(3)	O(4')–C(2)–C(21)	117.0(3)
C(1)–C(11)–C(12)	119.5(3)	C(2)–C(21)–C(22)	120.9(3)
C(1)–C(11)–C(16)	121.3(3)	C(2)–C(21)–C(26)	119.3(3)
C(12)–C(11)–C(16)	119.1(3)	C(22)–C(21)–C(26)	119.8(3)
C(11)–C(12)–C(13)	120.9(5)	C(21)–C(22)–C(23)	120.1(4)
C(12)–C(13)–C(14)	119.9(6)	C(22)–C(23)–C(24)	120.1(4)
C(13)–C(14)–C(15)	119.6(5)	C(23)–C(24)–C(25)	119.9(4)
C(14)–C(15)–C(16)	121.1(4)	C(24)–C(25)–C(26)	120.4(4)
C(11)–C(16)–C(15)	119.5(3)	C(21)–C(26)–C(25)	119.7(3)
Triphenylphosphine oxide group			
Cu–O(5)–P	142.5(1)	C(43)–C(44)–C(45)	119.9(4)
O(5)–P–C(31)	112.5(1)	C(44)–C(45)–C(46)	120.6(4)
P–C(31)–C(32)	118.2(2)	C(41)–C(46)–C(45)	120.1(3)
P–C(31)–C(36)	121.5(3)	O(5)–P–C(51)	114.0(1)
C(32)–C(31)–C(36)	120.2(3)	P–C(51)–C(52)	123.5(3)
C(31)–C(32)–C(33)	119.1(3)	P–C(51)–C(56)	117.1(3)
C(32)–C(33)–C(34)	120.3(4)	C(52)–C(51)–C(56)	119.4(3)
C(33)–C(34)–C(35)	120.8(4)	C(51)–C(52)–C(53)	120.2(4)
C(34)–C(35)–C(36)	119.6(5)	C(52)–C(53)–C(54)	120.7(4)
C(31)–C(36)–C(35)	120.1(4)	C(53)–C(54)–C(55)	119.4(5)
O(5)–P–C(41)	110.8(1)	C(54)–C(55)–C(56)	121.3(5)
P–C(41)–C(42)	122.1(2)	C(51)–C(56)–C(55)	119.0(4)
P–C(41)–C(46)	118.8(2)	C(31)–P–C(41)	106.3(1)
C(42)–C(41)–C(46)	119.0(3)	C(31)–P–C(51)	106.4(1)
C(41)–C(42)–C(43)	120.1(3)	C(41)–P–C(51)	106.4(1)
C(42)–C(43)–C(44)	120.3(4)		

not only in structure but also in the spin-exchange interaction between the two nuclear copper(II) atoms,[10] and have discussed the relation between the Cu...Cu distance and the spin-exchange interaction, measured by the "$-2J$" value.[10] The Cu...Cu distance of the present compound is 2.657(1) Å, which is comparable to that in *tetrakis(μ-formato-O,O')-bis(γ-picoline)dicopper(II)*, 2.665(1) Å.[10] The "$-2J$" value of the latter complex was reported as 507 cm^{-1},[10] which is essentially similar

to the value of $458\,cm^{-1}$ estimated by Melnik and Mrozinski for the present compound.[4]

In the Ph_3PO group, all bond distances and angles almost equal those of triphenylphosphine oxide itself[13] except for the P–O distance, which is slightly longer than that in the uncoordinated molecule (as observed in many complexes).[14] The angle at the bridging O atom of Ph_3PO ligand is found to be 142.5(1)°, which is comparable to that in cis-dichlorodioxobis(triphenylphosphine oxide)uranium(VI) (144.5°).[14] However, there is wide range variety of metal–O–P angles in Ph_3PO-coordinated complexes, according to the local molecular structure, and involving steric hindrance between adjacent bulky ligands.[14] The five phenyl rings are almost planar; maximum and average deviations of the ring carbon atoms are 0.01 and 0.0015 Å, respectively. All other bond distances and angles are within normal ranges.

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