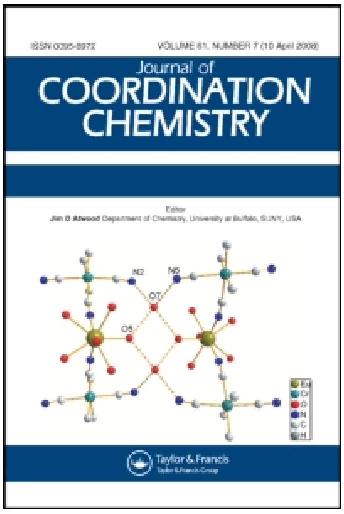

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Synthesis of a binuclear copper(I) complex $[Cu_2(PPh_3)_6(k\text{-}OOCH)](ClO_4)$ - insertion reaction of carbon dioxide

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Synthesis of a binuclear copper(I) complex $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$ – insertion reaction of carbon dioxide

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A novel binuclear complex $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$ (**II**) was synthesized via the interaction of carbon dioxide with $[Cu(PPh_3)_2(BH_4)]$ (**I**) in the presence of PPh_3 and $NBu_4(ClO_4)$. It was characterized by elemental analysis and spectroscopic methods as well as by single-crystal X-ray diffraction. Crystals are monoclinic, space group C_2/c, with $a = 25.911(5)$, $b = 13.6361(3)$, $c = 26.929(5)$ Å, $\beta = 90.21(3)°$, $V = 9323.1(3)$ Å^3, $Z = 8$ and $D_c = 1.314\,g\,cm^{-3}$. The formate ligand of **II** in the solid state displays a near-perfect linear coordination mode as CO_2 and serves as a bridge for the two $Cu(PPh_3)_3$ units with the O–C–O bond angle being 180.0(5)°. A mechanism involving carbon dioxide insertion into the Cu–H bond of $[Cu(PPh_3)_2(BH_4)]$ (**I**) for the formation of **II** is proposed.

Keywords: Carbon dioxide; Insertion; Linear formate ligand; Binuclear copper complex; Crystal structure

1. Introduction

Carbon dioxide is the most abundant carbon source on Earth [1]. In the face of a dramatic increase in mineral oil prices and the diminution of oil reserves, the search for alternative sources of energy has greatly intensified recently. One intriguing solution is the efficient conversion of carbon dioxide into useful carbon-containing feedstock. Carbon dioxide also represents the major gas responsible for the "greenhouse effect". Thus, the utilization of carbon dioxide might help to address this problem. In Nature, light-induced carbon dioxide fixation or reduction by green plants is the most important chemical process. Each year, roughly 2×10^{11} tons of glucose are formed [2].

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As one of the most important metals for biological systems, copper offers great chemical versatility in coordination geometries, binding ligands and valences [1–3]. Copper-containing proteins provide diverse biochemical functions, including biosynthesis of connective tissue (lysyl oxidase), catalysis of substrate oxygenation (dopamine β-monooxygenase), oxygen transport (hemocyanin) and electron transfer in photosynthesis (plastocyanin) [3]. In this context, we report herein the formation of the first linear binuclear formate copper complex, $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$, made from the reaction of carbon dioxide with a copper(I) tetrahydroborate, and its X-ray crystal structure and properties.

2. Experimental

2.1. *Materials and synthesis*

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. All solvents were dried by standard methods and distilled under nitrogen prior to use. $[Cu(PPh_3)_3(ClO_4)]$, $[Cu(PPh_3)_3(OOCH)]$ and $[Cu(PPh_3)_2(BH_4)]$ were prepared according to literature procedures [4].

2.2. *Physical measurements*

Copper and phosphorus content were determined using a JA96-975 ICP-AES instrument. FT-IR spectra were recorded on a Nicolet 170SX spectrophotometer. TG-DTA spectra were recorded on a PE-TGS-2 instrument. Conductivity measurements were carried out in MeOH solution at 25°C using a Shanghai DDS-11A conductometer and a DJS-1 type platinum black electrode. Melting points were determined on an Electrothermal apparatus. NMR spectra (^1H, ^{13}C and ^{31}P) were measured in $CDCl_3$ on a Bruker AV300 NMR spectrometer with TMS as reference for ^1H and ^{13}C and 85% H_3PO_4 as reference for ^{31}P. Electrospray mass spectra (ES-MS) were recorded on an LCQ system (Finngan MAT, USA) using methanol as the mobile phase. The spray voltage, tube lens offset, capillary voltage and capillary temperature were set at 4.5 kV, 20.0 V, 7.0 V and 200°C, respectively, and the quoted m/z values are for the major peaks in the isotope distribution. XPS spectra were recorded on a VG ESCALAB MK II instrument using Al Kα radiation. High voltage, electric current and vacuum were set at 12.5 kV, 20 mA and 6×10^{-8} mbar, respectively.

2.3. *Synthesis of $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$ (II)*

2.3.1. Method A. Carbon dioxide gas was bubbled into a mixture containing $[Cu(PPh_3)_2(BH_4)]$ (1 mmol, 0.603 g), PPh_3 (1 mmol, 0.262 g) and $NBu_4(ClO_4)$ (0.6 mmol, 0.205 g) in dichloromethane (90 cm^3) at room temperature for 3 h, followed by the addition of ethanol (30 cm^3). The title compound was then crystallized by partial evaporation of the solvent. Yield: 56%. m.p. 190°C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.10–7.90 (m, $P(C_6H_5)_3$), 8.56 (s, OOCH). Anal. Calc. (Found) for $C_{109}H_{90}ClCu_2O_6P_6$(%): C, 70.99 (70.64); H, 4.92 (4.87); P, 10.08 (9.90); Cu, 6.89 (6.70).

2.3.2. Method B. To a solution of $[Cu(PPh_3)_3(ClO_4)]$ (1 mmol, 0.949 g) in ethanol ($30\,cm^3$) was added with constant stirring a solution of $[Cu(PPh_3)_3(OOCH)]$ (1 mmol, 0.8945 g) in dichloromethane ($30\,cm^3$). The resulting colorless solution was subsequently allowed to evaporate slowly at room temperature to a final volume of 5–10 cm^3. Colorless crystals obtained were separated by filtration, washed with ethanol and dried under vacuum. Yield: 69%.

2.4. *X-ray data collection and structure determination of $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$ (II)*

A single crystal of dimensions 0.4 × 0.4 × 0.3 mm of the complex was selected and mounted on an automatic Enraf-Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator using Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 6476 unique reflections ($R_{int} = 0.1193$) was measured at room temperature with $3.02° < 2\theta < 46.18°$. No significant change was detected in the intensity of three standard reflections. Lorentz, polarization and absorption corrections were applied to the intensity data (empirical method, ω-scan). The structure was solved by direct methods and Fourier syntheses and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were generated geometrically and refined isotropically. A total of 561 parameters was refined. The final refinement converged at $R_1 = 0.0543$, $wR_2 = 0.1458$ for 6476 observed reflections with $I \geq 2\sigma(I)$, and $R_1 = 0.1065$, $wR_2 = 0.1859$ for all data. The largest final difference peak and hole were 0.818 and $-0.572\,e\,Å^3$, respectively. The function minimized was $w = 1/[\sigma^2 F_o^2 + (0.1000P)^2 + 0.0000P]$, where $P = 1/3(F_o^2 + 2F_c^2)$. Computations were performed using the SPD program on a P2P11/44 computer. Crystal data are given in table 1. Final atomic coordinates for all nonhydrogen atoms and equivalent thermal parameters are listed in table 2.

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{109}H_{90}ClCu_2O_6P_6$
Formula weight	1844.16
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *C*2/*c*
Unit cell dimensions	$a = 25.911(5)$ Å $b = 13.6361(3)$ Å, $\beta = 90.21(3)°$ $c = 26.929(5)$ Å
Volume	9323.1(3) $Å^3$
Z, Calculated density	8, 1.314 g/cm^3
Absorption coefficient	0.644 mm^{-1}
F(000)	3828
Crystal size	0.40 × 0.40 × 0.30 mm
θ range for data collection	1.51 to 23.09°
Index ranges	$-28 \leq h \leq 28$, $-14 \leq k \leq 0$, $-29 \leq l \leq 29$
Reflections collected/unique	12 915/6476 [*R*(int) = 0.1193]
Completeness to 2θ (23.09)	98.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6476/0/561
Goodness-of-fit on F^2	1.150
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0543$, $wR_2 = 0.1458$
R indices (all data)	$R_1 = 0.1065$, $wR_2 = 0.1859$
Largest diff. peak and hole	0.818 and $-0.572\,e\,Å^{-3}$

Table 2. Final nonhydrogen atomic coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Cu	1626(1)	2423(1)	822(1)	50(1)
P(3)	985(1)	3436(1)	472(1)	51(1)
P(1)	1957(1)	3031(1)	1570(1)	55(1)
P(2)	1491(1)	695(1)	852(1)	52(1)
C(64)	1352(2)	73(4)	264(2)	55(1)
C(84)	411(2)	3616(4)	854(2)	50(1)
C(23)	1804(2)	4317(5)	1737(2)	67(2)
O(1)	2226(2)	2497(4)	292(2)	97(2)
C(82)	−505(2)	3511(5)	1013(3)	80(2)
C(72)	301(2)	3459(6)	−907(2)	83(2)
C(74)	697(2)	3069(4)	−127(2)	53(1)
C(42)	940(2)	344(4)	1236(2)	55(1)
C(96)	1201(2)	4718(4)	350(2)	57(1)
C(73)	549(2)	3763(4)	−479(2)	67(2)
C(76)	343(2)	1771(5)	−635(2)	79(2)
C(75)	595(2)	2082(5)	−213(2)	67(2)
C(34)	1200(2)	2179(5)	2150(2)	71(2)
C(36)	2046(2)	1862(5)	2447(2)	77(2)
C(35)	1726(2)	2315(4)	2102(2)	59(1)
C(41)	931(2)	−474(5)	1551(2)	75(2)
C(83)	−87(2)	3412(4)	697(2)	66(2)
C(85)	469(2)	3952(5)	1342(2)	69(2)
C(63)	1679(3)	243(6)	−137(2)	91(2)
C(93)	1568(3)	6593(6)	107(3)	106(3)
C(15)	2659(2)	3039(5)	1652(2)	65(2)
C(94)	1111(3)	6501(5)	346(3)	91(2)
C(44)	78(2)	755(5)	1493(2)	74(2)
C(33)	996(3)	1630(5)	2533(2)	83(2)
C(31)	1836(3)	1294(6)	2826(3)	103(2)
C(52)	2024(2)	−84(4)	1091(2)	64(2)
C(86)	66(3)	4071(5)	1647(2)	82(2)
C(22)	1562(3)	4606(6)	2159(3)	93(2)
C(14)	2900(3)	3526(6)	2042(3)	103(3)
C(62)	1588(3)	−215(7)	−590(3)	115(3)
C(43)	510(2)	948(4)	1217(2)	63(2)
C(24)	1947(3)	5043(5)	1394(3)	100(2)
C(65)	933(2)	−535(5)	185(2)	74(2)
C(55)	2850(4)	−1179(9)	1468(4)	129(3)
C(46)	493(3)	−670(5)	1831(2)	84(2)
C(32)	1317(3)	1191(6)	2874(3)	93(2)
C(13)	3434(3)	3461(6)	2088(4)	105(3)
C(45)	73(2)	−73(6)	1800(2)	80(2)
C(26)	1592(5)	6320(9)	1912(6)	159(6)
C(53)	2344(4)	278(7)	1425(4)	174(6)
C(81)	−423(3)	3831(5)	1479(3)	87(2)
C(54)	2742(5)	−299(8)	1625(5)	203(7)
C(66)	848(3)	−989(5)	−274(3)	95(2)
C(71)	198(2)	2471(6)	−990(2)	80(2)
C(61)	1186(3)	−819(6)	−656(3)	97(2)
C(95)	922(2)	5553(4)	475(2)	71(2)
C(25)	1829(5)	6050(7)	1487(5)	150(5)
C(92)	1836(3)	5782(7)	1(4)	142(4)
C(21)	1467(4)	5618(8)	2238(4)	143(4)
C(56)	2523(4)	−1603(7)	1141(5)	138(4)
C(91)	1662(3)	4831(5)	107(3)	108(3)
C(51)	2109(3)	−1051(6)	944(4)	131(3)
C(16)	2954(3)	2521(8)	1329(3)	137(4)

(*continued*)

Table 2. Continued.

Atom	x/a	y/b	z/c	U(eq)
C(12)	3715(3)	2941(9)	1764(4)	130(3)
C(1)	2500	2500	0	133(6)
C(11)	3482(3)	2475(11)	1395(4)	199(7)
C1	0	6635(2)	2500	119(1)
O(3)	306(4)	6051(8)	2774(3)	228(4)
O(2)	317(7)	7195(12)	2323(11)	560(20)

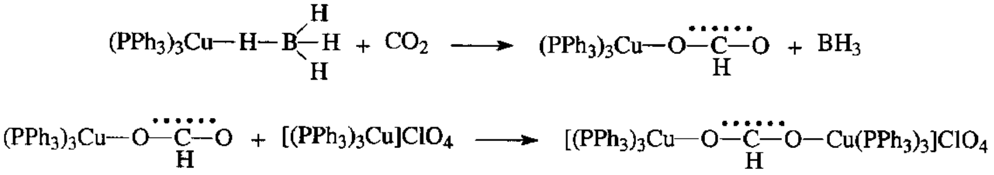
3. Results and discussion

3.1. *Synthesis and characterization of [$Cu_2(PPh_3)_6(\mu$-OOCH)](ClO_4) (II)*

There is considerable interest in the chemistry of metal formates as these compounds are considered as key intermediates in the catalytic reduction of carbon oxides [5]. The interaction of carbon dioxide with [$Cu(PPh_3)_2(BH_4)$] (**I**) in the presence of PPh_3 and $NBu_4(ClO_4)$ leads to the formation of a binuclear formate complex, [$Cu_2(PPh_3)_6(\mu$-OOCH)](ClO_4) (**II**), in high yield. Complex **II** is colorless, crystalline and diamagnetic, and fairly stable in air in the solid state; it is soluble in solvents such as CH_2Cl_2, $CHCl_3$ and acetonitrile but has limited solubility in methanol, ethanol, acetone and tetrahydrofuran, and is insoluble in toluene, ether and hexane. The electrospray mass spectrum of the complex exhibits two main peaks at $m/z = 587.2$ and 848.8, corresponding to $[Cu(PPh_3)]^+$ and $[Cu(PPh_3)_2]^+$, respectively. Molar conductivity measurement ($102\,S\,cm^2\,mol^{-1}$) indicated that the complex behaves as a univalent electrolyte in methanol solution. Elemental analysis results are in a good agreement with the proposed structure, which was further verified by the X-ray structure determination, an alternative synthesis of this binuclear formate, as well as spectroscopic characterization (*vide infra*).

The FT-IR spectrum (in CsI) of **II** shows the expected absorptions bands at 510m, 695m, 744s, 1434m, 1479m and 1600w cm^{-1}, due to the PPh_3 ligand; peaks at 622 and 1091 cm^{-1}, characteristic of perchlorate anion, appear. The P–Ph absorption observed at about 1100 cm^{-1}, which is higher in both frequency and intensity than for free PPh_3, indicates that the phosphine is coordinated to copper. Importantly, the presence of the formate group in **II** is clearly revealed by FI-IR with the observation of a strong asymmetric $\nu(CO_2)$ vibration at 1585 cm^{-1} and a weaker symmetric $\nu(CO_2)$ vibration at 1369 cm^{-1}. Typically, $\nu(CO_2)_{asym}$ is slightly lower in bidentate and bridging formate complexes than in monodentate species, whereas the opposite is true for $\nu(CO_2)_{sym}$. The strong band at 1585 cm^{-1} and the weak band at 1369 cm^{-1} are assignable to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$, respectively; the latter absorption supports a linear coordination mode of formate in **II**.

^1H NMR spectra of **II** display a singlet at 8.56 ppm, characteristic of the formate proton [6]. It is worth noting that the proton resonance of the formate ligand does not vary significantly with change of bonding mode [7]. ^{13}C NMR analysis of **II** shows a distinct resonance at δ 170.1 ppm, corresponding to the coordinated formate carbon [8], which is shifted to higher field than in formic acid ($\delta = 166.3$ ppm). XPS measurements offer information concerning copper–ligand binding. The P_{2p} binding energy in **II** is observed at 135.1 eV, larger than the corresponding value (P 133.9 eV)



Scheme 1. Proposed reaction pathway for the formation of **II** via the reaction of carbon dioxide and $[Cu(PPh_3)_2(BH_4)]$ (**I**) in the presence of PPh_3 and $NBu_4(ClO_4)$.

of free PPh_3, attributed to electronic density reduction at the P atom via the formation of the P → Cu bond in the complex. Its ^{31}P NMR spectrum recorded at room temperature displays a single resonance at $\delta = -4.1$ ppm, about 6 ppm downfield from that of free PPh_3 and comparable to that of the phosphine ligand in a similar copper(I) complex, $[Cu(PPh_3)_2Cl]$ (δ −3.85 ppm) [9]; the presence of a sharp singlet in the ^{31}P NMR spectrum indicates the fluxional nature of **II**.

TG-DTA thermograms of **II** reveal that the complex decomposes in one step from 190 to 560°C, corresponding to loss of PPh_3 and formate ligands, and giving CuO as the final residue (residue weight: experimental = 7.3% *vs.* calc. 8.6%). The DTA curve shows characteristic exothermic peaks at 190–560°C.

The formation of **II** from the reaction of carbon dioxide and $[Cu(PPh_3)_2(BH_4)]$ (**I**) in the presence of PPh_3 and $NBu_4(ClO_4)$ may involve two individual steps (scheme 1), based on the analogous chemistry of alkali-metal tetrahydroborates [10]. In the first step, carbon dioxide insertion into the Cu–H bond of **I** yields a copper formate complex, which couples further in the second step with $[Cu(PPh_3)_3(ClO_4)]$, generated *in situ*, to form the binuclear formate complex **II**. This mechanism was reinforced and independently verified by the fact that the reaction of $[Cu(PPh_3)_3(ClO_4)]$ and $[Cu(PPh_3)_3(OOCH)]$, the two proposed intermediates, indeed gives **II** in high yield.

3.2. *Crystal structure of* $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$

The structure of **II** was further elucidated by single-crystal X-ray diffraction. Selected bond lengths and angles are given in table 3. The molecular structure of the complex is depicted in figure 1. The structure of $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$ consists of discrete binuclear cations $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)]^+$ and perchlorate anions. The structure of the complex shows some disorder, but it no doubt contains $[Cu(PPh_3)_3(\mu\text{-}OOCH)]$ units containing a four-coordinate metal center with three crystallographically independent PPh_3 ligands occupying three of the coordination sites and the formate anion coordinated through one oxygen atom at the fourth site. The formic acid molecule in $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$ is unlike the corresponding copper(I) complex $[Cu(PPh_3)_3(OOCH)]$ [11], in which formate is coordinated by one oxygen atom. Concerning the formate group, the O–C–O bond angle is 180.0(5)°. The structure of the complex also shows that it contains symmetry-related $Cu(PPh_3)_3$ units bridged by formate. The metal coordination geometry is distorted tetrahedral as evidenced by the values of the P–Cu–O angles, ranging from 100.40(14) to 107.24(15)°. Cu–P bond lengths range from 2.3346(16) to 2.3373(14) Å and are similar to values recorded for a range of other $[Cu(PPh_3)_3X]$ complexes [12,13]. Cu–P bond distances [2.3346(16)

Table 3. Selected bond distances (Å) and angles (°) for the complex.

Cu–O(1)	2.116(5)	O(1)–Cu–P(1)	107.24(15)
Cu–P(1)	2.3346(16)	O(1)–Cu–P(2)	100.40(14)
Cu–P(2)	2.3373(16)	O(1)–Cu–P(3)	103.01(14)
Cu–P(3)	2.3373(14)	P(1)–Cu–P(2)	111.57(5)
C(1)–O(1)	1.061(5)	P(1)–Cu–P(3)	113.87(6)
Cl–O(2)	1.210(13)	P(3)–Cu–P(2)	118.70(5)
Cl–O(3)	1.333(8)	C(1)–O(1)–Cu	174.0(4)
		O(1)A–C(1)–O(1)	180.0(5)

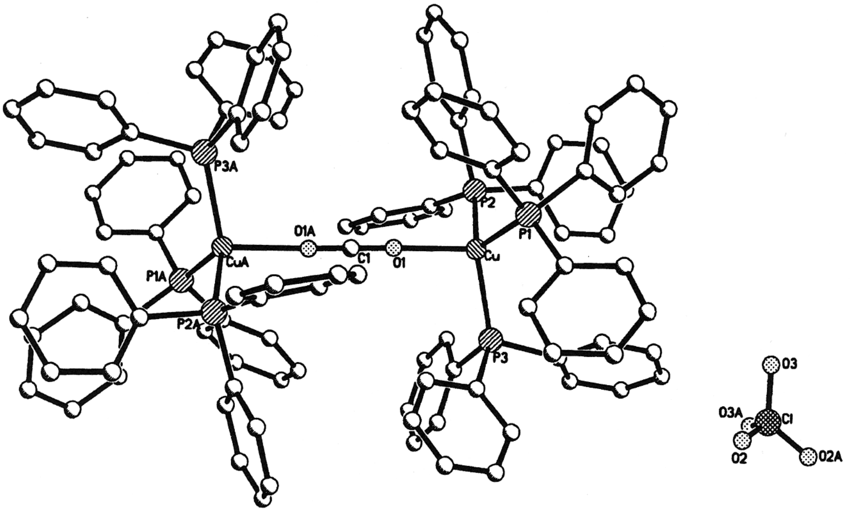


Figure 1. X-ray structure of the complex $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$. Hydrogen atoms are omitted for clarity.

to 2.3373(14) Å] fall within the usual range for copper–PPh_3 compounds so far synthesized: 2.240(2)–2.283(2) Å in $[(Ph_3P)_2CuO_2CCH_2CN]_2$, 2.245(1)–2.271(1) Å in $[Cu(phen)(PPh_3)_2]^+$ and 2.225(2)–2.246(2) Å in $[WCu_3(O)S_3(C_4H_{10}O_2PS_2)(PPh_3)_3]$. The Cu···Cu separation in this complex [5.936(5) Å] is significantly longer than the sum of van der Waals radii for copper (2.8 Å), suggesting that the copper atoms in the present compound are not involved in metal–metal interaction. P–Cu–P angles (average 114.71°) are larger than the corresponding values (average 94.9°) reported for [(triphos)Cu(OOCH)] [14], due to three separate triphenylphosphine ligands occupying more space. In the latter compound the triphos ligand and the monodentate formate ligand show very similar coordination geometry around the copper atom. The bridging group Cu–O–C–O–Cu is almost in line [Cu–O–C 174.0(4)°], leading to a larger distance between copper atoms and less congestion in the ligands. Concerning the formate ligand, the C(1)–O(1) bond distance is 1.061(5) Å. The observed Cu–O distance of 2.116(5) Å is somewhat larger than the distance [2.015(9) Å] found in [Cu(triphos)(HCOO)] due to the presence of μ-OOCH in $[Cu_2(PPh_3)_6$ $(\mu\text{-}OOCH)]$ (ClO_4). With respect to the associated phenyl moieties, they are quite coplanar.

In summary, the novel, symmetrical binuclear complex $[Cu_2(PPh_3)_6(\mu\text{-}OOCH)](ClO_4)$ has been structurally characterized by single-crystal X-ray methods and found to contain a bidentate linear formate ligand, in which IR absorptions of formate agree with the observed structures for these types of compounds.

Supplemental material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 223950. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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