



# Synthesis and Crystal Structure of a Copper(II) Benzoate Complex Bearing a Bis-2,2'-Tetrahydrofuryl Peroxide Moiety

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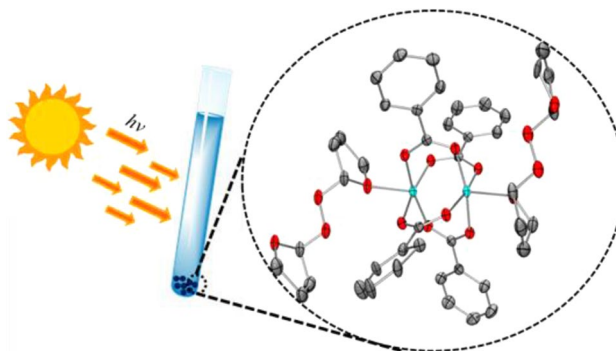
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## Abstract

Complex  $[\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF} - (\eta^1\text{-O}_2)]_\infty$  (**2**) (ben =  $\text{C}_6\text{H}_5\text{CO}_2^-$  benzoate; THF = tetrahydrofuran) was isolated when a solution of  $\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}$  (**1**) in THF upon natural sunlight irradiation yields crystals suitable for single-crystal X-ray diffraction analysis. **2**, crystallized in the  $C2/c$  monoclinic space group,  $Z=8$ ,  $V=3394.2(4) \text{ \AA}^3$ , and the unit cell parameters  $a=9.7935(7) \text{ \AA}$ ,  $b=19.0055(13) \text{ \AA}$ ,  $c=18.2997(13) \text{ \AA}$ ,  $\alpha=90^\circ$ ,  $\beta=94.7996(11)^\circ$  and  $\gamma=90^\circ$ . This is the first example of a polymeric copper(II) carboxylate compound stabilizing a peroxo group via its apical ligand (THF molecule). Additionally, **2** was also characterized by elemental analysis, Fourier-transformed infrared spectroscopy (FTIR) and Raman spectroscopy.

## Graphical Abstract

Upon sunlight irradiation a solution of  $\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}$  (ben =  $\text{C}_6\text{H}_5\text{CO}_2^-$ , benzoate; THF = tetrahydrofuran) in THF yields  $[\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF} - (\eta^1\text{-O}_2)]_\infty$  as a polymeric copper(II) carboxylate compound stabilizing a peroxo group via its apical ligand (THF molecule).



**Keywords** Copper(II) benzoate · Tetrahydrofuryl peroxide · Coordination complex · Sunlight-promoted reaction · Peroxide formation

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## Introduction

Carboxylate moiety  $\text{RCO}_2^-$  acts as versatile ligand adopting different configuration such as *syn-syn*, *syn-anti* or *anti-anti* (Fig. 1). The *syn-syn* conformation allows the formation of binuclear compounds, while *syn-anti* and *anti-anti* arrangements favor layered or chain structures [1–3].

Interestingly, copper(II) carboxylate complexes usually exhibit a *syn-syn* geometry having a dimeric-like structure featuring a paddle-wheel array with four carboxylate fragments acting as bridging ligand without the presence of a copper–copper bonding interaction. In fact, bond distances are about 2.44–2.81 Å resulting in a weak coupling between the unpaired electrons in each Cu(II) ion, associated with an antiferromagnetic coupling between the metals [4–6]. Furthermore, the apical position around each copper atom can be occupied either by donor solvent molecules like ethanol [1], water [7, 8], tetrahydrofuran [9], or by other ligands [10–13].

On the other hand, copper-bearing carboxylate complexes have shown multifarious applications spanning from catalyst for the oxidation of alcohols or phenols [14, 15], activation of C–C bonds [16], water oxidation catalyst [17], fungal and microbial activity [18, 19], and as a source of blue light in fireworks [20].

In the pursuit of copper(II) benzoate complexes with different apical donors that can bind to Si(100) surface [21, 22] aimed at evaluating their potential as catalysts toward water oxidation, we isolated the complex  $[\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF} - (\eta^1-\text{O}_2)]_\infty$  (**2**) (ben =  $\text{C}_6\text{H}_5\text{CO}_2^-$ , benzoate; THF = tetrahydrofuran) when  $\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}$  (**1**) was exposed to natural sunlight, rendering a novel compound with a tetrahydrofuryl peroxide (THFPO) moiety. Herein, we report on the synthesis, spectroscopic characterization, and X-ray crystal structure of **2**.

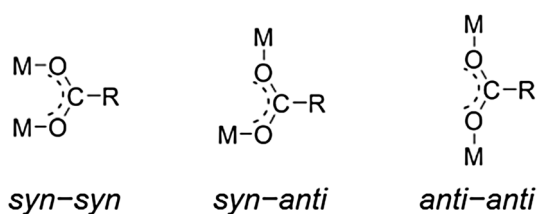


Fig. 1 Coordination modes for the carboxylate  $\text{RCO}_2^-$  moiety

## Experimental

### General Methods and Materials

The following chemicals: sodium benzoate (Sigma Aldrich,  $\geq 99.5\%$ ) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Across Organics) were used as received. Compound **1** was prepared by variations on the literature procedure [7]. THF (Fisher, 99.9% HPLC grade) was purified with the M-Braun solvent drying system. Infrared spectra were recorded in a FTIR-ATR Scientific Evolution Nicolet 6700 instrument in the range 4000–650  $\text{cm}^{-1}$ . UV–Vis was obtained in a Thermo Scientific Evolution 600 UV–Vis instrument. Induce coupled plasma atomic emission spectroscopy (ICP–AES) measurements were performed at Centro de Electroquímica y Energía Química, CELEQ; Universidad de Costa Rica on a Perkin Elmer Plasma 400 Emission Spectrometer with optical detector. The samples were first digested in nitric acid to dissolve them and the results were obtained from comparison with a calibration curve. The elemental analysis was performed at the Analytisches Labor der Anorganischen Chemie der Universität Göttingen, Germany.

### Synthesis of $\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}$ (**1**)

A reaction mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.43 g; 2.5 mmol) and sodium benzoate (0.73 g; 5 mmol) in THF (40 mL) was refluxed for 12 h, giving a blue solution and a precipitate. After vacuum filtration, the resulting blue solution was concentrated under vacuum to give a blue solid. Yield 0.66 g (70%, 1.75 mmol). FTIR-ATR ( $\text{cm}^{-1}$ ): 2968 (w); 2889 (w); 1679 (w); 1625 (m); 1571 (m); 1492 (w); 1403 (s); 1281 (w); 1176 (w); 1039 (m); 1025 (m); 937 (w); 915 (w); 841 (w); 725 (s); 711 (s) (w = weak, m = medium, s = strong). UV–Vis (5 mM in THF):  $\lambda_{\text{max}} = 685$  nm,  $A_{\text{max}} = 1.009$ ;  $\epsilon = 201$  L mol $^{-1}$  cm $^{-1}$ .

### Synthesis of $[\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF} - (\eta^1-\text{O}_2)]_\infty$ (**2**)

**1** (0.22 g, 0.60 mmol) was dissolved in dry THF (15 mL), and the resulting blue solution was slowly evaporated at room temperature and under natural sunlight. Blocklike blue microcrystals were obtained after one and a half month in quantitative yield. FTIR-ATR ( $\text{cm}^{-1}$ ): 2953 (w), 2359 (w), 1769 (w), 1671 (m), 1599(w), 1570 (m), 1529 (w), 1492 (w), 1401 (s), 1260 (w), 1188 (w), 1112 (w), 1022 (w), 976 (w), 904 (w), 842 (w), 718 (s), 683 (s). Raman ( $\text{cm}^{-1}$ ): 850 (s, O–O). (w = weak, m = medium, s = strong). Anal. Calc. for  $\text{C}_{18}\text{H}_{17}\text{CuO}_6$ : C, 55.0; H, 4.5; Cu, 16.2. Found C, 54.6; H, 4.7; Cu, 17.0.

## Crystal Structure Determination

Single crystals of compound **2** were selected from the mother solution and covered with perfluorinated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using the X-Temp2 device [23, 24]. The data of compound **2** were collected at 100k on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and INCOATEC Mo- $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) microfocus source [25] with INCOATEC Quazar mirror optics. All data were integrated with SAINT [26] and semi-empirical absorption corrections were applied with SADABS [27]. The structure was solved by direct methods (SHELXS-97) [28] and refined against all data by full-matrix least-squares methods on  $F^2$  (SHELXL2013) [29, 30] inside the SHELXLE GUI [31]. All non-hydrogen-atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined on calculated positions using a riding model. Their  $U_{\text{iso}}$  values were constrained to 1.5  $U_{\text{eq}}$  of their pivot atoms for terminal  $sp^3$  carbon atoms and 1.2 times for all other carbon atoms. The positions of these three hydrogen atoms were freely refined with  $U_{\text{iso}}$  values constrained to 1.2  $U_{\text{eq}}$  of its pivot atom. The disordered groups were refined using geometry (SAME) and  $U_{ij}$  restraints (SIMU, RIGU) implemented in SHELXL. The crystallographic data are given in Table 1. The selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) are presented in Table 2. All the bond lengths and angles of **2** are shown in the Electronic Supplementary Material (ESM) Table S1.

## Results and Discussion

### Synthesis of $\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}$ (**1**) and $[\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF} - (\eta^1 - \text{O}_2)]_\infty$ (**2**)

The preparation of compound **1** proceeds by metathesis reaction of sodium benzoate salt and copper(II) chloride under reflux in THF (Scheme 1).

During the experiments to obtain crystals of complex **1**, a solution of THF was left evaporating slowly in air and ambient temperature; furnishing single crystals after about one and a half month. To our surprise, complex **2** was unexpectedly attained, displaying an intriguing bis-2,2'-tetrahydrofuryl peroxide (THFPO) moiety in the axial position, based on the X-ray measurements (Scheme 2). **2**, is a polymeric complex soluble in THF but insoluble in diethyl ether and dichloromethane.

To our knowledge, **2** represents the first example of a Cu(II) bimetallic system with a peroxo fragment in axial position. Aiming at improving the synthesis of **2**, different procedures were tested, namely, bubbling both oxygen gas (previously dried with anhydrous  $\text{CaCl}_2$ ) and dry air into a solution of **1** in THF at  $-5 \text{ }^\circ\text{C}$  and ambient temperature,

**Table 1** Crystallographic parameters and refinement data for complex **2**

Chemical formula	$\text{C}_{18}\text{H}_{17}\text{CuO}_6$
$M_r$	392.86
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
$a, b, c$ ( $\text{\AA}$ )	9.7935 (7); 19.0055 (13); 18.2997 (13)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	94.7996 (11)
$\gamma$ ( $^\circ$ )	90
$V$ ( $\text{\AA}^3$ )	3394.2 (4)
$Z$	8
$F(000)$	1616
Radiation type	Mo $K\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	1.32
Crystal size (mm)	$0.14 \times 0.10 \times 0.05$
$\theta$ ( $^\circ$ ) range for data collection	2.2–28.4
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	29,203, 4282, 3719
$R_{\text{int}}$	0.028
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.670
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.026; 0.065; 1.03
No. of reflections	4282
No. of parameters	301
No. of restraints	652
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.36; $-0.30$

**Table 2** Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for compound **2**

Bond lengths ( $\text{\AA}$ )			
Cu1–O2	1.9532 (11)	Cu1–O5	2.2335 (11)
Cu1–O3	1.9552 (11)	Cu1–Cu1 <sup>i</sup>	2.5785 (4)
Cu1–O4 <sup>i</sup>	1.9616 (11)	O6–O6 <sup>ii</sup>	1.483 (3)
Cu–O1 <sup>i</sup>	1.9765 (11)		
Bond angles ( $^\circ$ )			
O4–Cu1–O1 <sup>i</sup>	169.19 (4)	O4–C8A–O3	125.42 (14)
O5–Cu1–Cu1 <sup>i</sup>	173.61 (3)	C11A–C12A–C13A	120.49 (17)
C15–O6–O6 <sup>ii</sup>	105.37 (14)		

Symmetry codes: (i)  $-x+1, y, -z+1/2$ ; (ii)  $-x+3/2, -y+1/2, -z+1$

nonetheless this led to the decomposition of the benzoate ligand possibly because of the high oxidant conditions. We successfully replicated the synthesis of **2** when it was exposed to natural sunlight. In this regard, it is well-known that the  $\alpha$  position of ethers readily undergo autoxidation reactions to form peroxides, promoted by long exposure to air, heat and light [32–34]. This autoxidation reaction of ethers can be catalyzed by the presence of metals, such as

iron [35, 36], nickel [37, 38] or cobalt [39, 40]. In our case the presence of these metals was ruled out by analyzing the chemical composition of precursor **1** with inductively coupled plasma atomic emission spectroscopy (ICP–AES), so that one could suggest that the formation of the peroxy synthon could be mediated by the copper atom (Table S2).

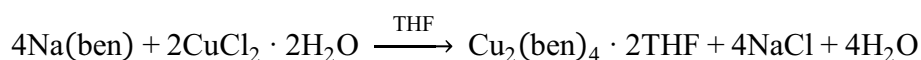
### Crystal Structure of $[\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}-(\eta^1-\text{O}_2)]_\infty$ (**2**)

**2**, crystallizes in a monoclinic  $C2/c$  space group; the metallic centers are coordinated with four benzoate ligands through the oxygen atoms in a bidentate fashion (Fig. 2a). The complex has a Cu–Cu distance of 2.5786(7) Å (Table 2), which can be considered a weak interaction between the copper atoms ( $\text{Cu} \cdots \text{Cu}$ ), and compares well with the Cu–Cu distance in **1** of 2.607 Å [9].

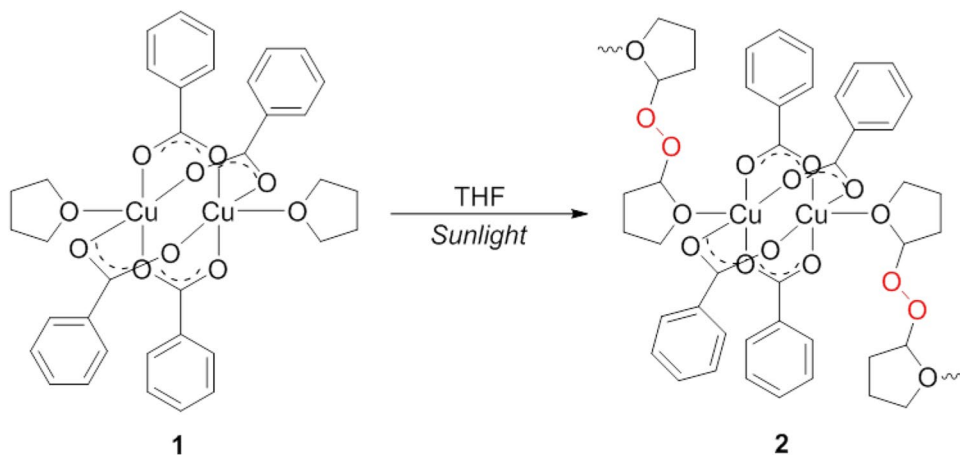
Moreover, the geometry around each copper atom is square pyramidal with the oxygen atoms of the benzoate ligand occupying the basal position and the THFPO in apical position. The bond length Cu1–O5 [2.2337(12) Å] and the average bond distance Cu–O<sub>benzoate</sub> (1.962 Å) are similar to complex **1** [9]. In addition, the bond distance O6–O6 in THFPO (1.484(2) Å), is in good agreement to the average bond length O–O in the free peroxide (1.482 Å) [41].

Thus far, there is only one compound crystallographically characterized featuring a THFPO group reported by Shur and coworkers, containing mercury atoms with the chemical formula  $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2(\text{THFPO})\}$  [42], whose O–O bond distance is similar to **2**. In the former case, the oxygen atoms from the THF molecules cooperatively bind to the mercury centers, whereas in **2** they tether covalently

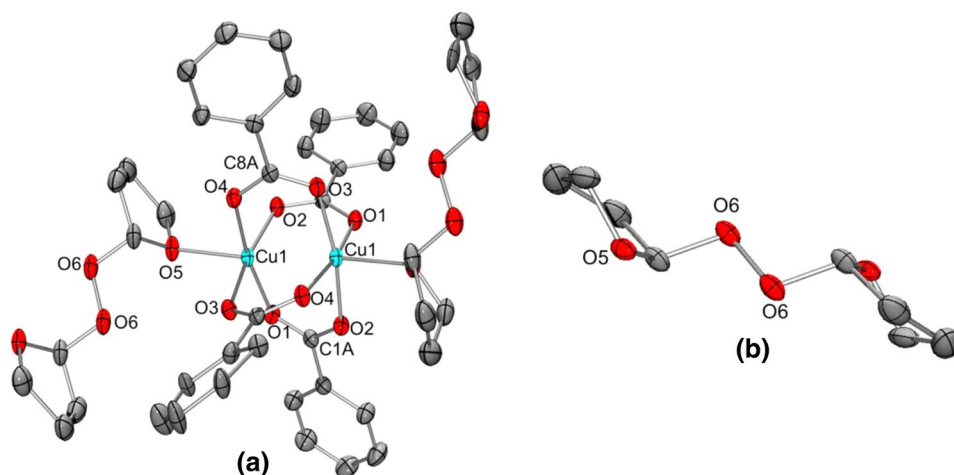
**Scheme 1** Synthesis of  $\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}$  (**1**)



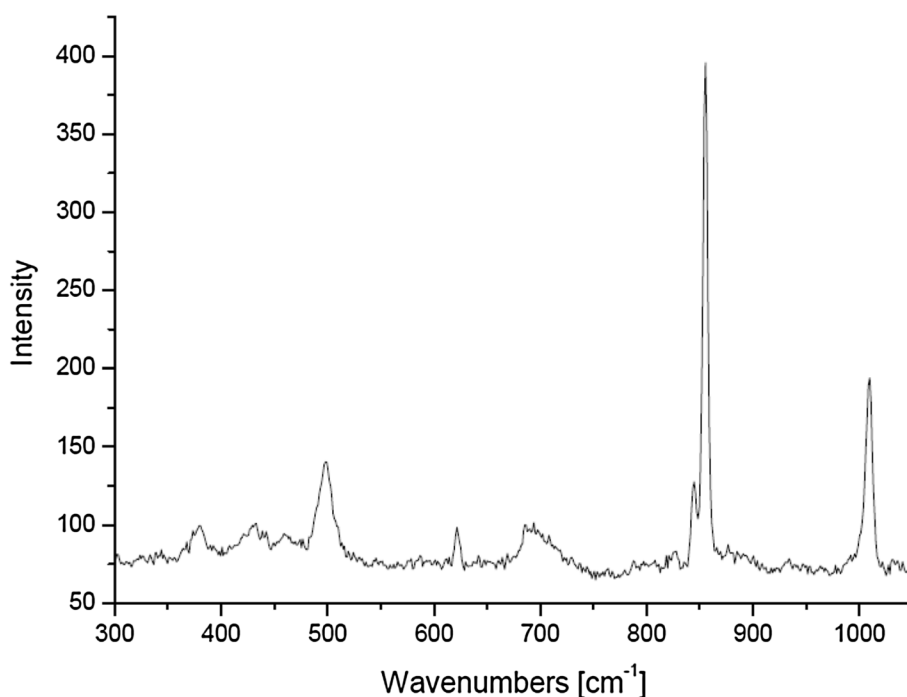
**Scheme 2** Synthesis of complex **2**



**Fig. 2** **a** Fragment of the polymeric chains in compound **2** with thermal ellipsoids at 50% probability. **b** Detail of the tetrahydrofuryl peroxide moiety (H atoms omitted for clarity)



**Fig. 3** Raman spectrum of complex **2**



to the Cu atoms. For both compounds the THFPO moiety adopts an “envelope” conformation (Fig. 2b).

### Infrared and Raman Spectra of $[\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF} - (\eta^1\text{-O}_2)]_\infty$ (**2**)

Infrared spectrum (IR) of **2** shows bands at 2953 and 2894  $\text{cm}^{-1}$  ascribed to the stretching of the C–H in the THF group; and the bands at 1571 and 1492  $\text{cm}^{-1}$  can be assigned to asymmetric  $\nu_{\text{as}}$  and symmetric  $\nu_{\text{sym}}$  stretching of the carboxylate group, respectively (Fig. S1). Since the difference  $\Delta\nu = \nu_{\text{as}} - \nu_{\text{sym}} < 200 \text{ cm}^{-1}$ , compound **2** probably shows a bidentate *syn-syn* configuration in the  $\text{RCOO}^-$  ligand [43, 44]. Based on Raman spectroscopy, the vibration of the  $\nu(\text{O}-\text{O})$  bond can be assigned at 850  $\text{cm}^{-1}$  (Fig. 3), while in the IR appears as a weak signal at 853  $\text{cm}^{-1}$ .

These vibrational bands are comparable to other molecules having a peroxo moiety, for instance, benzoyl peroxide exhibits  $\nu(\text{O}-\text{O})$  vibration bond at 846 and 847  $\text{cm}^{-1}$  for the IR and Raman spectra, respectively [45].

## Conclusion

In summary, we report the first copper benzoate complex with a THFPO group in the apical position. Interestingly, this polymeric complex can stabilize an  $\text{O}_2^{2-}$  fragment formed when a solution of  $\text{Cu}_2(\text{ben})_4 \cdot 2\text{THF}$  in THF is exposed to sunlight, showing the facile autoxidation process of ethers under these reaction conditions.

Our findings would offer the possibility to clarify the mechanism underlying the oxidation of ethers as to whether the oxygen atoms come from a water molecule, molecular oxygen or from both sources. This could be determined by monitoring a reaction with isotopically labeled water or oxygen.

## Supplementary Material

CCDC 1433811 contains the supplementary crystallographic data for **2**. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk>, or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1 EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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