Two Copper Complexes Based on Pyrazole-3-carboxylic Acid as Heterogeneous Catalysts for Highly Selective Oxidation of Alkylbenzenes Postprint

Authors: JIANG Xiu-Yan, RONG Nian-Xin, QIAN Rui, QIU Tian-Tian, YAO Qing-Xia, Xian-Qiang Huang

Date: 2017-11-05T00:00:00+00:00

Abstract

Two new copper complexes based on pyrazole-3-carboxylic acid (H2pca) ligand, Cu(Hpca)2(H2O)2 · 2H2O (1) and Cu2(pca)2(H2O)4 (2) have been synthesized and fully characterized by single-crystal X-ray diffraction (SXRD), infrared spectroscopy (IR), thermal gravity analysis (TGA), powder X-ray diffraction (PXRD) and elemental analyses. Complex 1 is mononuclear while complex 2 shows a dinuclear structure. Complex 1 crystallizes in the monoclinic system, space group P21/c with Z = 2, a = 6.5591(5), b = 21.696(2), c = 4.9486(2) Å, V = 680.94(9) Å3, F(000) = 366, Dc = 1.745 g/cm3, = 1.650 mm-1, the final R = 0.0340 and wR = 0.0792. Complex 2 crystallizes in the monoclinic system, space group P21/n with Z = 2, a = 5.1935(4), b = 9.6052(7), c = 12.7347(9) Å, V = 634.44(8) Å3, F(000) = 420, Dc = 2.195 g/cm3, = 3.404 mm-1, the final R = 0.0305 and wR = 0.0653. The three-dimensional frameworks of two complexes are formed by the O—H ··· O and N—H ··· O hydrogen bonding interactions. Notably, two copper complexes are further used as catalysts in the oxidation of alkylbenzenes using t-butylhydroperoxide (TBHP) as the oxidant and they exhibit excellent catalytic performance (Conv. up to 98.9%, Sele. up to 98.7%).

Full Text

Preamble

Two Copper Complexes Based on Pyrazole-3-carboxylic Acid as Heterogeneous Catalysts for Highly Selective Oxidation of Alkylbenzenes

JIANG Xiu-Yan (蒋秀燕)[1], RONG Nian-Xin (荣念新)[2], QIAN Rui (钱瑞)[2], QIU Tian-Tian (邱田田)[2], YAO Qing-Xia (姚清侠)[2], HUANG Xian-Qiang (黄现强)[2]

[1] School of Chemical Engineering, Shengli College, China University of Petroleum, Dongying 257061, China
[2] Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry & Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, China

Abstract

Two new copper complexes based on the pyrazole-3-carboxylic acid (H_2pca) ligand, $Cu(Hpca)_2(H_2O)_2 \cdot 2H_2O$ (1) and $Cu_2(pca)_2(H_2O)_4$ (2), have been synthesized and fully characterized by single-crystal X-ray diffraction (SXRD), infrared spectroscopy (IR), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), and elemental analysis. Complex 1 is mononuclear while complex 2 exhibits a dinuclear structure. Complex 1 crystallizes in the monoclinic system, space group $P2_1/c$ with Z = 2, a = 6.5591(5), b = 21.696(2), c = 4.9486(2) Å, V = 680.94(9) Å^3, F(000) = 366, Dc = 1.745 g/cm^3, = 1.650 mm^{-1}, with final R = 0.0340 and wR = 0.0792. Complex 2 crystallizes in the monoclinic system, space group $P2_1/n$ with Z = 2, a = 5.1935(4), b = 9.6052(7), c = 12.7347(9) Å, V = 634.44(8) Å^3, F(000) = 420, Dc = 2.195 g/cm^3, = 3.404 mm^{-1}, with final R = 0.0305 and wR = 0.0653. The three-dimensional frameworks of both complexes are formed through O—H $\cdots$ O and N—H $\cdots$ O hydrogen bonding interactions. Notably, the two copper complexes were further employed as catalysts in the oxidation of alkylbenzenes using t-butylhydroperoxide (TBHP) as the oxidant, and they exhibited excellent catalytic performance (conversion up to 98.9%, selectivity up to 98.7%).

Keywords: copper complexes; crystal structure; oxidation of alkylbenzenes
DOI: 10.14102/j.cnki.0254-5861.2011-1731

1. Introduction

In recent decades, transition-metal complexes have attracted sustained attention due to their unique structures and extensive applications in catalysis, adsorption, electrical conducting materials, magnetic and optical materials, and related fields [1-4]. Among transition metals, copper is particularly important in coordination chemistry, catalytic chemistry, and as a micronutrient essential for life [5-8]. Its flexible coordination modes readily enable the formation of mononuclear, dinuclear, and multinuclear complexes [9,10]. Pyrazole carboxylates serve as versatile multifunctional ligands that play a crucial role in generating excellent architectures because of several advantages: first, these multidentate organic ligands possess potential coordination nodes and strong coordination ability, exhibiting diverse chelating and bridging modes; second, pyrazole carboxylates act as multiple proton donors and acceptors, enabling the construction of high-dimensional supramolecular frameworks through hydrogen-

bonding or π-π stacking interactions. However, few examples of transition-metal complexes based on 1H-pyrazole-3-carboxylic acid have been reported, likely due to the presence of only one carboxyl group in the ligand [11-13]. Consequently, synthesizing such pyrazole-3-carboxylic acid complexes and developing their catalytic activities for organic reactions remains a significant challenge.

Herein, we report the syntheses and structural characterizations of a mononuclear copper complex (1) and a dinuclear copper complex (2), obtained under room temperature conditions or via hydrothermal methods. Both complexes have been fully characterized by SXRD, PXRD, elemental analysis, TGA, and FT-IR spectroscopy. Complexes 1 and 2 were subsequently investigated as catalysts for the oxidation of alkylbenzenes using TBHP as an oxidant.

2. Experimental

2.1 Instruments and Reagents

All reagents and solvents were purchased from commercial sources and used without further purification. PXRD patterns were recorded on a Shimadzu XRD-6000 instrument using monochromatized Cu-Kα radiation (λ = 1.54178 Å) at 40 kV and 50 mA, scanning from 4° to 50° (2) at 298 K. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet 170 SXFT/IR spectrometer. GC analyses were performed on a Shimadzu GC-2014C equipped with an FID detector and an Rtx-1701 Sil capillary column. TGA experiments were conducted on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 °C/min from room temperature to 600 °C under nitrogen atmosphere.

2.2 Synthesis of Complex $Cu(Hpca)_2(H_2O)_2 \cdot 2H_2O$ (1)

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.2 mmol) in 5 mL of distilled water was slowly added to a stirred solution containing H_2pca (0.0448 g, 0.4 mmol) and NaOH (0.1 mL, 1 M in H_2O) in 5 mL of distilled water. The reaction mixture was stirred for 1 h at room temperature and then filtered. Blue block crystals of 1 were obtained by slow evaporation of the filtrate at room temperature over three weeks (yield: 32% based on Cu). IR (KBr, cm^{-1}): 3484 (s), 3363 (s), 1660 (s), 1555 (m), 1507 (m), 1475 (m), 1382 (m), 1355 (s), 1263 (s), 1232 (w), 1133 (m), 1068 (s), 1014 (m), 942 (m), 898 (m), 839 (m), 785 (m), 649 (m), 502 (w). Anal. calcd for $C_8H_{14}CuN_4O_8$: C 26.86, H 3.94, N 15.66%. Found: C 26.91, H 3.97, N 15.54%.

2.3 Synthesis of Complex $Cu_2(pca)_2(H_2O)_4$ (2)

A mixture of H_2pca (0.0448 g, 0.4 mmol), $CuCl_2 \cdot 2H_2O$ (0.068 g, 0.4 mmol), NaOH (0.2 mL, 1 M in H_2O), and distilled water (10 mL) was sealed in a 23 mL Teflon-lined steel vessel and heated at 150 °C for 72 h, then cooled to room

temperature at 0.1 °C/min. The resulting blue block crystals of 2 were collected and washed with distilled water (yield: 31% based on Cu). IR (KBr, cm^{-1}): 3485 (s), 1659 (s), 1557 (w), 1512 (m), 1475 (m), 1382 (s), 1356 (s), 1263 (s), 1232 (w), 1133 (m), 1068 (m), 1014 (m), 942 (m), 898 (m), 838 (m), 785 (m), 649 (w), 497 (w). Anal. calcd for $C_8H_{12}Cu_2N_4O_8$: C 22.91, H 2.88, N 13.36%. Found: C 22.98, H 2.95, N 13.27%.

2.4 Procedure for Catalytic Oxidation of Alkylbenzenes

Alkylbenzene (0.25 mmol), copper complex (5 mol%), 70% TBHP (0.625 mmol), and benzonitrile (2 mL) were added to a 10 mL flask, and the reaction was carried out at 70 °C for 24 h. After completion, the mixture was analyzed by GC-MS and GC.

2.5 Reuse Experiments

Reuse experiments were performed for the oxidation of diphenylmethane under optimal conditions. After the reaction, the catalyst was recovered by filtration (5.8 mg, 96% recovery), washed with MeOH (ca. 3 × 5 mL), and air-dried before reuse. The PXRD spectrum of the recovered catalyst matched that of the fresh catalyst (Fig. 6 [Figure 6: see original paper]). The recovered catalyst was reused for a second oxidation run; after completion, it was again recovered by filtration (5.5 mg, 95% recovery), washed with MeOH (ca. 3 × 5 mL), and air-dried. A third run was prepared identically, achieving 95.7% conversion of diphenylmethane as determined by GC. The PXRD spectrum of the catalyst after the third run remained identical to that of the fresh catalyst (Fig. 6).

2.6 Structure Determination

Single-crystal X-ray diffraction data for complexes 1 and 2 were collected at 296 K on a Bruker-AXS CCD diffractometer using MoKα radiation (λ = 0.71073 Å) and a multi-scan technique. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL 97 crystallographic software package [14,15]. Final refinements included anisotropic displacement parameters for all atoms. Selected bond lengths, bond angles, and hydrogen bond parameters for 1 and 2 are listed in Tables 1 and 2, respectively.

3. Results and Discussion

3.1 Structure Description of $Cu(Hpca)_2(H_2O)_2 \cdot 2H_2O$ (1)

Single-crystal X-ray diffraction reveals that complex 1 contains one crystallographically independent Cu^{2+} ion, one $Hpca^-$ anion, and one coordinated water molecule. As shown in Fig. 1a [Figure 1: see original paper], the Cu^{2+} ion is coordinated by two oxygen atoms and two nitrogen atoms (O(1), O(1A), N(1) and N(1A)) from two $Hpca^-$ anions, and two oxygen atoms (O(3), O(3A)) from

two coordinated water molecules, adopting a distorted $\{CuO_4N_2\}$ octahedral geometry. The Cu—O and Cu—N bond distances are 1.9901(19)–2.508(2) Å and 1.976(2) Å, respectively, consistent with reported copper complexes [16]. Bond angles around the Cu^{2+} ion range from 81.44(8)° to 180.00(5)°. The $Hpca^-$ anion adopts a chelating coordination mode wherein one oxygen atom and one nitrogen atom coordinate to adjacent Cu^{2+} ions, forming a five-membered ring. Adjacent mononuclear units are linked by two types of hydrogen bonding interactions to form a 1D supramolecular chain: the first involves oxygen atoms (O(3)) of coordinated water molecules and carboxylic oxygen atoms (O(1)) of $Hpca^-$ anions (O(3)—H(3C)$\cdots$O(1) = 2.737(5) Å), and the second involves oxygen atoms (O(3)) and nitrogen atoms (N(2)) of pyrazole rings from $Hpca^-$ anions (N(2)—H(2)$\cdots$O(3) = 2.733(4) Å) (Fig. 1b [Figure 1: see original paper]). These chains are further connected by O(3)—H(3D)$\cdots$O(2) (2.687(0) Å) hydrogen bonds between coordinated water molecules and carboxylic oxygen atoms (O(2)) to construct a 2D supramolecular layer (Fig. 1c [Figure 1: see original paper]). Notably, 1D water chains are formed by O(4)—H(4D)$\cdots$O(4) (2.814(3) Å) hydrogen bonding interactions. Additional hydrogen bonding (O(4)—H(4C)$\cdots$O(2) = 2.888(7) Å) between carboxylic oxygen atoms (O(2)) of the 2D layers and these water chains further stabilizes the structure, leading to a 3D supramolecular architecture (Fig. 1d [Figure 1: see original paper]).

3.2 Crystal Structure of $Cu_2(pca)_2(H_2O)_4$ (2)

Single-crystal X-ray data reveal that the asymmetric unit of 2 consists of one Cu^{2+} cation, one pca^{2-} anion, and two coordinated water molecules (Fig. 2a [Figure 2: see original paper]). The Cu^{2+} ion is five-coordinated by one oxygen atom (O(1)) and one nitrogen atom (N(1)) from one pca^{2-} anion, one nitrogen atom (N2) from a second pca^{2-} anion, and two coordinated water molecules (O(3), O(4)), forming a $\{CuO_3N_2\}$ tetragonal pyramidal geometry. The Cu—O and Cu—N bond distances are 1.9684(17)–2.3624(18) Å and 1.9521(19)–1.9628(19) Å, respectively. Bond angles around the Cu^{2+} ion range from 81.98(7)° to 172.52(8)°. The pca^{2-} anion adopts a monodentate-chelating coordination mode that connects Cu^{2+} ions to generate a dinuclear structure, wherein two pyrazole rings from adjacent pca^{2-} anions are parallel (dihedral angle = 0°) with a Cu$\cdots$Cu distance of 3.9060 Å. Four pyrazole nitrogen atoms and two Cu^{2+} ions are nearly coplanar, forming a six-membered ring. These dinuclear units are linked into a 1D supramolecular chain by O–H$\cdots$O hydrogen bonds between oxygen atoms (O(3)) of coordinated water molecules and carboxyl oxygen atoms (O(1)) of pca^{2-} anions (2.720(2) Å) (Fig. 2b [Figure 2: see original paper]). The final 3D supramolecular architecture is constructed through O(4)—H(8)$\cdots$O(3), O(3)—H(6)$\cdots$O(2), and O(4)—H(7)$\cdots$O(2) hydrogen bonding interactions between neighboring 1D chains (distances = 2.729(2), 2.749(2), and 2.736(3) Å, respectively) (Fig. 2c [Figure 2: see original paper]).

3.3 PXRD Analysis

The experimental and simulated PXRD patterns of complexes 1 and 2 are shown in Fig. 3 [Figure 3: see original paper]. The peak positions are in good agreement, confirming the phase purity of both complexes.

3.4 Thermal Stability Analysis

TGA was performed to evaluate the thermal stabilities of complexes 1 and 2 (Fig. 4 [Figure 4: see original paper]). For complex 1, a weight loss of 19.98% from room temperature to 105 °C (calculated 20.12%) corresponds to the loss of lattice and coordinated water molecules, followed by complete decomposition at 410 °C, leaving CuO as the residual. Complex 2 shows an initial weight loss of 16.69% at 90 °C (calculated 17.17%) due to departure of coordinated water molecules, then remains stable until 225 °C. Complete framework collapse occurs above 395 °C.

3.5 Selective Oxidation of Alkylbenzenes Catalyzed by Complexes 1 and 2

The oxidation of C−H bonds in alkylbenzenes is a powerful method for producing high-value chemical feedstocks from inexpensive raw materials, and significant efforts have been devoted to developing new catalysts [17]. In this context, converting benzylic hydrocarbons into valuable compounds has received considerable attention [18]. Herein, we report the oxidation of alkylbenzenes using TBHP as oxidant and two copper complexes as catalysts.

To evaluate the effectiveness of complexes 1 and 2, diphenylmethane was first examined as a standard substrate with 70% TBHP in benzonitrile at 80 °C for 24 h (Scheme 1). Conversion and selectivity data are summarized in Fig. 5 [Figure 5: see original paper]. After preliminary optimization, complex 2 demonstrated higher activity and selectivity for diphenylmethane oxidation compared to other tested catalysts.

Given its excellent performance, complex 2 was selected to examine long-term stability in a heterogeneous system. After reaction completion, the catalyst was easily separated by filtration, reactivated by washing with methanol, and reused directly in subsequent runs. The results show no significant activity loss after three cycles (conversion: 96.2% (1st), 96.0% (2nd), 95.7% (3rd)) (Fig. 5 [Figure 5: see original paper]). PXRD spectra of catalyst 2 collected before and after catalytic reactions confirm that the structure is maintained under turnover conditions (Fig. 6 [Figure 6: see original paper]).

The mild reaction conditions, excellent stability, and high yield for diphenylmethane oxidation to benzophenone prompted us to extend the substrate scope for complex 2 as a heterogeneous catalyst. As shown in Table 3 , complex 2 exhibits excellent catalytic activity for oxidizing diphenylmethane, 9H-xanthene, fluorene, and fluorene derivatives to the corresponding aryl ketones with yields

up to 97.6% (Table 3, entries 1-5). Compared to previous reports, complex 2 outperforms some heterogeneous catalysts such as polyoxometalates [19] and MOFs [20] for the oxidation of diphenylmethane, fluorene, and 9H-xanthene.

4. Conclusion

In summary, by controlling reaction conditions, we have synthesized two pyrazole-3-carboxylic acid complexes (1 and 2). The incorporation of Cu^{2+} cations enhances the stability of both complexes, enabling their use as heterogeneous catalysts for the selective oxidation of alkylbenzenes with high catalytic activity. Specifically, complex 2 efficiently converts alkylbenzenes to the corresponding aromatic ketones and can be reused by filtration without activity loss. Investigations into other potential catalytic applications of these complexes are ongoing.

References

(a) Zhang, J. P.; Zhang, Y. B.; Lin, J. B.; Chen, X. M. Metal azolate frameworks: from crystal engineering to functional materials. Chem. Rev. 2012, 112, 1001-1033; (b) Jiang, X. Y.; Rong, N. X.; Wang, G. D.; Cui, C. S.; Huang, X. Q. An imidazole-functionalized dioxovanadium complex with the highly selective oxidation of sulphides. Chin. J. Struct. Chem. 2017, 36, 429-437.

(b) Yin, Y.; Tan, Z.; Hu, L.; Yu, S.; Liu, J.; Jiang, G. Isotope tracers to study the environmental fate and bioaccumulation of metal-containing engineered nanoparticles: techniques and applications. Chem. Rev. 2017, 117, 4462-4487; (b) Han, C. B.; Wang, Y. L.; Liu, Q. Y. Crystal structure and magnetic properties of a dinuclear terbium compound $Tb_2(\mu_2\text{-anthc})_4(anthc)_2(1,10\text{-phen})_2$. Chin. J. Struct. Chem. 2017, 36, 705-710.

(3) Paskevicius, M.; Jepsen, L. H.; Schouwink, P.; Černý, R; Ravnsbæk, D. B.; Filinchuk, Y.; Dornheim, M.; Besenbacher, F.; Jensen T. R. Metal borohydrides and derivatives -synthesis, structure and properties. Chem. Soc. Rev. 2017, 46, 1565-1634.

(4) Zhao, Y.; Li, Z.; Sharma, U. K.; Sharma, N.; Song, G.; Eycken, E. V. V. Copper-catalyzed alkylarylation of activated alkenes using isocyanides as the alkyl source: an efficient radical access to 3,3-dialkylated oxindoles. Chem. Commun. 2016, 52, 6395-6398.

(5) Žilić, D.; Rakvin, B.; Milić, D.; Pajić, D.; Đilović, I. Crystal structures and magnetic properties of a set of dihalo-bridged oxalamidato copper(II) dimers. Dalton Trans. 2014, 43, 11877-11887.

(6) Teong, S. P.; Yu, D.; Sum, Y. N.; Zhang, Y. Copper catalysed alkynylation of tertiary amines with CaC_2 via sp^3 C–H activation. Green Chem. 2016, 18, 3499–3502.

(7) Tirsoaga, A.; Cojocaru, B.; Teodorescu, C.; Vasiliu, F.; Grecu, M. N.; Ghica, D.; Parvulescu, V. I.; Garcia, H. C–N cross-coupling on supported copper catalysts: the effect of the support, oxidation state, base and solvent. J. Catal. 2016, 341, 205–220.

(8) Niu, M.; Li, Z.; Li, X.; Huang, X. Two chiral alkanolamine Schiff base Cu(II) complexes as potential anticancer agents: synthesis, structure, DNA/protein interactions, and cytotoxic activity. RSC Adv. 2016, 6, 98171–98179.

(9) He, J.; Yin, Y. G.; Wu, T.; Li, D.; Huang, X. C. Design and solvothermal synthesis of luminescent copper(I)-pyrazolate coordination oligomer and polymer frameworks. Chem. Commun. 2006, 2845–2847.

(10) Fernandes, T. A.; Santos, C. I. M.; André, V.; Kłak, J.; Kirillova, M. V.; Kirillov, A. M. Copper(II) coordination polymers self-assembled from aminoalcohols and pyromellitic acid: highly active precatalysts for the mild water-promoted oxidation of alkanes. Inorg. Chem. 2016, 55, 125–135.

(11) Artetxe, B.; Reinoso, S.; Felices, L. S.; Vitoria, P.; Pache, A.; Martín-Caballero, J.; Gutiérrez-Zorrilla, J. M. Functionalization of krebs-type polyoxometalates with N,O-chelating ligands: a systematic study. Inorg. Chem. 2015, 54, 241–245.

(12) López-Viserasa, M. E.; Fernández, B.; Hilfiker, S.; González, C. S.; González, J. L.; Calahorro, A. J.; Colacio, E.; Rodríguez-Diéguez, A. In vivo potential antidiabetic activity of a novel zinc coordination compound based on 3-carboxy-pyrazole. J. Inorg. Biochem. 2014, 131, 64–67.

(13) Liu, G. N.; Zhu, W. J.; Chu, Y. N.; Li, C. C. Three d^{10} metal coordination compounds based on pyrazole-3-carboxylic acid showing mixed-ligand characteristic: syntheses, crystal structures, and photoluminescent properties. Inorg. Chim. Acta 2015, 425, 28–35.

(14) Sheldrick, G. M. SHELXS-97, Program for X-ray Crystal Structure Solution. University of Göttingen, Germany 1997.

(15) Brese, N. E.; O' Keeffe, M. Bond-valence parameters for solids. Acta Crystallogr. Sect. B 1991, 47, 192–197.

(16) Li, B.; Zhao, J. W.; Zheng, S. T.; Yang, G. Y. Hydrothermal synthesis and structure of di-copper(II)-complex substituted monovacant polyoxotungstate with a 1D chain structure. Inorg. Chem. Commun. 2008, 11, 1288–1291.

(17) Chen, H.; Deng, Y.; Yu, Z.; Zhao, H.; Yao, Q.; Zou, X.; Bäckvall, J. E.; Sun, J. 3D Open-framework vanadoborate as a highly effective heterogeneous pre-catalyst for the oxidation of alkylbenzenes. Chem. Mater. 2013, 25, 5031–5036.

(18) Shi, D.; Ren, Y.; Jiang, H.; Lu, J.; Cheng, X. A new three-dimensional metal-organic framework constructed from 9,10-anthracene dibenzoate and Cd(II) as a highly active heterogeneous catalyst for oxidation of alkylbenzenes. Dalton Trans. 2013, 42, 484–491.

(19) Yang, X. L.; Xie, M. H.; Zou, C.; He, Y.; Chen, B.; O' Keeffe, M.; Wu, C. D. Porous metalloporphyrinic frameworks constructed from metal 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin for highly efficient and selective catalytic oxidation of alkylbenzenes. J. Am. Chem. Soc. 2012, 134, 10638–10645.

(20) He, Q. T.; Li, X. P.; Chen, L. F.; Zhang, L.; Wang, W.; Su, C. Y. Nano-sized coordination cages incorporating multiple Cu(I) reactive sites: host-guest modulated catalytic activity. ACS Catal. 2013, 3, 1–9.

Scheme 1. Oxidation of diphenylmethane to benzophenone with TBHP

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

Complex 1		Complex 2	
Cu(1)-N(1)a	1.976(2)	Cu(1)-N(2)	1.9521(19)
Cu(1)-O(1)a	1.9901(19)	Cu(1)-O(4)	1.9684(17)
Cu(1)-O(1)	1.9901(19)	Cu(1)-O(1)	1.9899(17)
Cu(1)-O(3)	2.508(2)	Cu(1)-O(3)	2.3624(18)
Cu(1)-N(1)	1.976(2)	Cu(1)-N(1)	1.9628(19)
Cu(1)-O(3)	2.508(2)		

Angle	Complex 1	Angle	Complex 2
N(1)a-Cu(1)-N(1)	180.00(5)	N(2)-Cu(1)-N(1)	98.00(8)
N(1)-Cu(1)-O(1)a	98.56(8)	N(1)-Cu(1)-O(4)	168.42(8)
N(1)-Cu(1)-O(1)	81.44(8)	N(1)-Cu(1)-O(1)	81.98(7)
N(1)a-Cu(1)-O(3)	87.91(8)	N(2)-Cu(1)-O(4)	92.61(8)
N(1)a-Cu(1)-O(1)a	81.44(8)	N(2)-Cu(1)-O(1)	172.52(8)

Angle	Complex 1	Angle	Complex 2
N(1)a-Cu(1)-O(1)	98.56(8)	N(1)-Cu(1)-O(3)	92.73(7)
O(1)a-Cu(1)-O(1)	180.00(11)	O(1)-Cu(1)-O(3)	90.91(7)
O(1)a-Cu(1)-O(3)	89.09(7)	O(4)-Cu(1)-O(1)	92.09(8)
O(1)-Cu(1)-O(3)	88.94(7)	O(4)-Cu(1)-O(3)	86.89(7)
N(1)-Cu(1)-O(3)	90.27(7)		

Symmetry code: a: -x+1, -y+1, -z+3

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

D–H ⋯ A	d(D–H)	d(H ⋯ A)	d(D ⋯ A)
Complex 1			
N(2)-H(2) ⋯ O(3)a			2.733(4)
O(3)-H(3C) ⋯ O(1)b			2.737(5)
O(3)-H(3D) ⋯ O(2)c			2.687(0)
O(4)-H(4C) ⋯ O(2)d			2.888(7)
O(4)-H(4D) ⋯ O(4)e			2.814(3)
Complex 2			
O(3)—H(5) ⋯ O(1)			2.720(2)
O(3)—H(6) ⋯ O(2)			2.749(2)
O(4)—H(7) ⋯ O(2)			2.736(3)
O(4)—H(8) ⋯ O(3)			2.729(2)

Symmetry codes: a: -x+1, -y+1, -z+2; b: x, y, z-1; c: -x, -y+1, -z+3; d: -x, -y+1, -z+3; e: x, -y+3/2, z+1/2

Table 3. Results of Selective Oxidation of Benzylic Compounds Catalyzed by Complex 2 Using TBHP Oxidant[a]

Entry	Substrates	Conv. (%)	Products	Sele. (%)[b]

[a] Reaction conditions: substrates (0.25 mmol), complex 2 (5 mol%), TBHP (0.625 mmol), benzonitrile (2 mL), 80 °C, 24 h.
[b] Selectivity to ketones was analyzed by GC using naphthalene as internal standard. The by-products are corresponding alcohols, which were analyzed by GC-MS.

Fig. 1. (a) Coordination environment of the Cu^{2+} ions in 1 (hydrogen atoms and lattice water molecules omitted for clarity). (b) 1D supramolecular chain of 1 formed by hydrogen bonds along the c-axis. (c) 2D supramolecular layer of

1 formed by hydrogen bonds in the ac plane. (d) 3D supramolecular framework of 1 consisting of 1D water chains

Fig. 2. (a) Coordination environment of the Cu^{2+} ions in 2 (hydrogen atoms omitted for clarity). (b) 1D supramolecular chain of 2 formed by hydrogen bonds along the a-axis. (c) 3D supramolecular framework of 2 formed by hydrogen-bonding interactions

Fig. 3. Powder X-ray diffraction patterns of complexes 1 and 2

Fig. 4. TGA curves for complexes 1 and 2

Fig. 5. Conversion of diphenylmethane to benzophenone with different catalysts. Reaction conditions: diphenylmethane (0.25 mmol), catalysts (5 mol%), 353 K, TBHP (0.625 mmol), benzonitrile (2 mL), 24 h. a) Blank; b) $CuCl_2$ (10 mol%); c) complex 1 (10 mol%); d) complex 2 (5 mol%); e) 1st run; f) 2nd run; g) 3rd run

Fig. 6. PXRD spectra of complex 2 after three catalytic cycles

Note: Figure translations are in progress. See original paper for figures.