

Synthesis, structure and catalase-like activity of new dicopper(II) complexes with phenylglyoxylate and benzoate ligands

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Abstract

The preparation and characterization of dimeric $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ (bpy: 2,2'-bipyridine; phgaH: phenylglyoxylic acid) and $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ (baH: benzoic acid) complexes are described. Crystallographic characterization of the $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ complex has shown that the coordination geometry around copper(II) ions is distorted square pyramidal (monoclinic, $P21/c$, $a = 11.7440(4) \text{ \AA}$, $b = 20.9020(10) \text{ \AA}$, $c = 9.3980(10) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 93.2240(10)^\circ$, $\gamma = 90.00^\circ$, $V = 2303.3(3) \text{ \AA}^3$, $Z = 4$). These complexes were found to exhibit catalase-like activity.
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Keywords: Copper; Catalase; Kinetics; Carboxylates; X-ray structure

1. Introduction

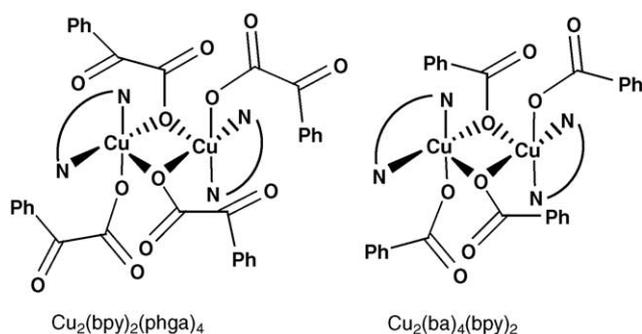
Oxidative stress has been defined as 'a disturbance in the pro-oxidant–antioxidant balance in favor of the former, leading to potential damage' [1]. The major oxidative stress produced by superoxide, however, is derived from its participation in peroxyxynitrite formation [2] and its involvement in the iron-catalyzed Haber–Weiss reaction (superoxide-driven Fenton chemistry [3]) causing hydrogen peroxide to be converted to hydroxyl radical. Hydroxyl radical, peroxyxynitrite and peroxyxynitrite-derived products (hydroxyl radical, carbonate radical and nitrogen dioxide) all have the potential to react with and damage most cellular targets including lipids, proteins, and DNA [4]. Enzymatic antioxidants regulate superoxide concentration by dismutation of superoxide to hydrogen peroxide (superoxide dismutase [5]), which is then converted to water (peroxidases such as glutathione peroxidase) or dismutated to water and dioxygen. Elimination of hydrogen peroxide is therefore critical to the efficacy of SOD

in reducing oxidative stress. Catalase and glutathione peroxidase serve this purpose. A number of manganese containing catalases have been isolated and characterized [6–8].

The direct utilization of this natural enzyme as a pharmaceutical agent is limited because of low membrane permeability as a consequence of its high molecular weight. So considerable efforts were made in order to obtain non-toxic, low molecular weight biomimetic molecules, which are able to catalyze the dismutation of superoxide anion and/or destroy the forming hydrogen peroxide.

A variety of low molecular weight complexes of transition metals, especially those of manganese, were prepared and studied as Mn-catalase mimetic complex systems [9–18]. Examples of such complexes include derivatives of anti-inflammatory drugs salicylates, aminoacids, peptides, and amines. Compared with $\text{Mn}_2(\text{II})$ model complex systems, $\text{Cu}_2(\text{II})$ systems reported are relatively rare [19–21]. Several binuclear copper(II) carboxylates of anti-inflammatory drugs such as salicylates [22], indomethacin [23], and lornalozac [24] were studied as SOD mimics, but none of simple carboxylates such as benzoate and phenylglyoxylate. In addition, it is known that the presence of coordination sites

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Scheme 1.

belonging to nitrogen heteroatomic rings such as imidazoles or pyridines is important for high SOD activity [25], and complexes with bipyridines and phenanthroline are DNA intercalators, showing ability to inhibit nucleic acid synthesis *in vivo* [26].

In this paper, we report the synthesis and structure of the binuclear copper(II) complexes $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ and $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ (Scheme 1). The catalase activity of these binuclear compounds have been measured in order to get insight into the mechanism of the H_2O_2 dismutation process in biological systems.

2. Experimental

2.1. Materials

All manipulations were performed under a pure dinitrogen or argon atmosphere unless otherwise stated, using standard Schlenk-type inert gas techniques [27]. Solvents used for the reactions were purified by literature methods [28] and stored under argon. $\text{Cu}(\text{OMe})_2$ was prepared according to the literature [29]. All other chemicals were commercial products and were used as received without further purification.

2.2. Analytical measurements

Infrared spectra were recorded on a Specord 75 IR (Carl Zeiss) spectrophotometer using samples mullied in Nujol between KBr plates or in KBr pellets. UV–vis spectra were recorded on a Shimadzu UV-160 spectrophotometer using quartz cells. Microanalyses were done by the Microanalytical Service of the University.

2.3. Synthesis of $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$

A solution of 601 mg (4 mmol) of phenylglyoxylic acid and 312 mg (2 mmol) 2,2'-bipyridine in 3 cm³ acetonitrile was added to a suspension of 251 mg (2 mmol) $\text{Cu}(\text{OMe})_2$ in 3 cm³ acetonitrile. The resulting blue suspension was stirred at 293 K for 2 h, filtered and kept for slow evaporation to obtain crystals suitable for X-ray structure determination. Yield:

73% (753 mg). Anal. Calcd. for $\text{Cu}_2\text{O}_{12}\text{C}_{52}\text{H}_{36}\text{N}_4$: C, 60.3; H, 3.5; N, 5.4. Found: C, 59.6; H, 3.7; N, 5.6.

2.4. Synthesis of $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$

A solution of 489 mg (4 mmol) of benzoic acid and 312 mg (2 mmol) 2,2'-bipyridine in 5 cm³ acetonitrile was added to a suspension of 251 mg (2 mmol) $\text{Cu}(\text{OMe})_2$ in 5 cm³ acetonitrile. The resulting blue suspension was stirred at 293 K for 2 h, filtered and kept for slow evaporation to obtain blue crystals. Yield: 71% (652 mg). Anal. Calcd. for $\text{Cu}_2\text{O}_{12}\text{C}_{52}\text{H}_{36}\text{N}_4$: C, 62.4; H, 3.9; N, 6.1. Found: C, 61.8; H, 3.7; N, 5.9.

2.5. Study of catalase-like activity

All reactions were carried out at 20 °C in a 50 cm³ reactor containing a stirring bar under air. Acetonitrile (30 cm³) was added to the complex (0.05 mmol) and the flask was closed with a rubber septum. Hydrogen peroxide (5 mmol) was injected through the septum with a syringe. The reactor was connected to a graduated burette filled with water and dioxygen evolution was measured volumetrically at time intervals of 0.5 min. Observed initial rates were expressed as mol dm⁻³ s⁻¹ by taking the volume of the solution (30 cm³) into account and calculated from the maximum slope of curve describing evolution of O₂ versus time.

2.6. X-ray structure determination of $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$

Single crystals of $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ suitable for an X-ray diffraction study were grown from acetonitrile upon standing at room temperature for a few days. The intensity data were collected with a Nonius Kappa CCD single-crystal diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. Crystallographic data and details of the structure determination are given in Table 1. SHELX-97 [30,31] was used for structure solution and full matrix least squares refinement on F^2 . Crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC 267818).

3. Results and discussion

3.1. Spectroscopic and single crystal X-ray structural characterization

3.1.1. FT-IR and UV–vis

In the visible range, a weak and broad band was discovered for these complexes at 679 and 697 nm for complexes $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ and $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$, respectively. These bands can be assigned to copper(II) d–d transitions. Another CT band was also observed at ca. 310 nm which can be attributed to N → Cu(II) or O → Cu(II) charge transfer. The positions of these bands are comparable with those found for

Table 1
Summary of the crystallographic data and structure parameters for $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$

Formula weight	517.96
Crystal system	Monoclinic
Crystal description	Blue prism
Space group	$P21/c$
Unit cell dimensions	
a (Å)	11.7440(4)
b (Å)	20.9020(10)
c (Å)	9.3980(10)
α (°)	90.00
β (°)	93.2240(10)
γ (°)	90.00
Volume (Å ³)	2303.3(3)
Z	4
Calculated density (g cm ⁻³)	1.494
Crystal size (mm ³)	$0.3 \times 0.2 \times 0.15$
Index ranges	$-14 \leq h \leq 14$ $-25 \leq k \leq 0$ $0 \leq l \leq 10$
Temperature (K)	293(2)
Radiation	Mo K α ($\lambda = 0.71073$)
Absorption coefficient (mm ⁻¹)	0.994
$F(000)$	1060
Reflections collected	4353
Observed reflections	3621
$[I > 2\sigma(I)]$	
Goodness-of-fit	1.143
Final R indices	$R_1 = 0.0521^a$, $wR_2 = 0.1204^b$
R indices (all data)	$R_1 = 0.0664$, $wR_1 = 0.1288$
Largest difference	
Peak/hole	0.423/−0.289

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w(|F_o|)^2} \right]^{1/2}$$

structurally known binuclear copper(II) valproate with pyridine [32].

The IR spectra for complex $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ and $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ exhibit two $\nu_{\text{asym}}(\text{CO}_2)$ and two $\nu_{\text{sym}}(\text{CO}_2)$ stretching bands, indicating the presence of two carboxylate ligands involved in different coordination modes. The 1605 and 1380 cm⁻¹ ($\Delta\nu = 225$ cm⁻¹) pair are assigned to the carboxyl group that acts as monodentate ligand [33,34], and the 1555 and 1397 cm⁻¹ ($\Delta\nu = 158$ cm⁻¹) pair are assigned to the other carboxylate that acts as asymmetric monodentate, bridging ligand [35–37]. These results are consistent with the proposed binuclear structures containing CuN_2O_3 chromophores. The stretching vibrations corresponding to those typical of coordinated bpy occur at 730, 830, 1030, 1232 and 1600 cm⁻¹ [38,39]. The band at 1652 cm⁻¹ in case of $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ can be assigned to the $\nu(\text{CO})$ group.

3.1.2. X-ray structure

$\text{Cu}_2(\text{bpy})_2(\text{phga})_4$: an ORTEP plot showing the atom numbering scheme employed is given in Fig. 1.

This complex is a dimer. Three oxygen and two nitrogen atoms are coordinated around each copper ion in the distorted square-pyramidal arrangement ($\tau = 0.01$ [40]), thus

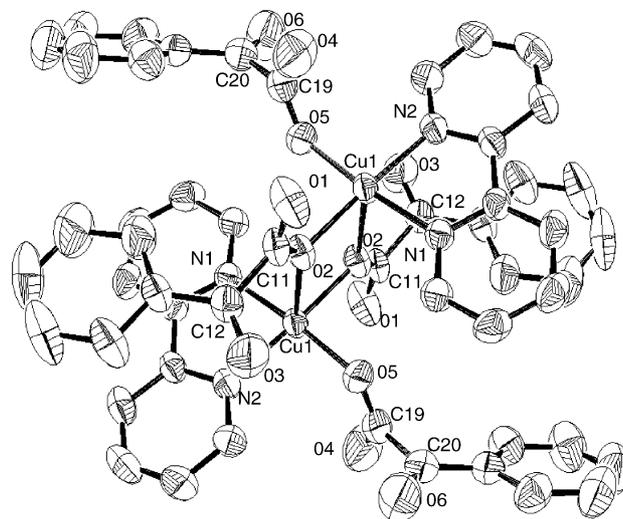


Fig. 1. Ellipsoid drawing of $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ with the atom numbering scheme.

forming a CuN_2O_3 chromophore in both cases. Each copper(II) ion is in 4 + 1 environment with O(2), O(5), N(1), N(2) in the basal plane and O(2) from the another bridging carboxylate in the axial position. The in-plan Cu–O bond distances average 1.945 Å and Cu–N bond distances 2.000 Å, which are in the normal range [33,37,41–43]. The axial Cu–O bond distance (2.383(2) Å) is significantly longer. The values of O(2)–Cu(1)–N(2) and O(2)–Cu(1)–O(2) bond angles (175.40(10) and 76.37(9) Å, respectively) reflect the distorted square pyramidal geometry surrounding the copper ion. The copper–copper separation is 3.432 Å in the dinuclear complex, which is longer than the van der Waals distances for two copper atoms (2.86°). Selected bond lengths and bond angles of the complex are listed in Table 2.

3.2. Kinetic studies

The catalytic decomposition of hydrogen peroxide has been studied as a model reaction for the catalase enzymes. The kinetic studies on the disproportionation of H_2O_2 into H_2O and O_2 were carried out by the method of initial rates monitoring the increase of the evolved dioxygen and it was found that the copper complexes $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ and

Table 2
Selected bond lengths (Å) and bond angles (°) for $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$

Cu(1)–O(5)	1.918(2)	Cu(1)–O(2)	1.971(2)
Cu(1)–N(2)	1.998(3)	Cu(1)–N(1)	2.003(3)
Cu(1)–O(2)	2.383(2)	N(2)–C(6)	1.352(4)
O(1)–C(11)	1.215(4)	O(2)–C(11)	1.273(4)
O(3)–O(12)	1.207(4)	O(4)–C(19)	1.220(5)
O(5)–C(19)	1.238(5)	O(6)–C(20)	1.218(5)
N(1)–C(5)	1.343(4)	N(1)–C(1)	1.343(4)
N(2)–C(10)	1.339(4)		
O(5)–Cu(1)–O(2)	90.10(10)	O(5)–Cu(1)–N(2)	94.36(11)
O(2)–Cu(1)–N(2)	175.40(10)	O(5)–Cu(1)–N(1)	174.69(11)
O(2)–Cu(1)–N(1)	94.57(10)	N(2)–Cu(1)–N(1)	80.92(11)
O(2)–Cu(1)–O(2)	76.37(9)	O(5)–Cu(1)–O(2)	88.61(10)

Table 3
Kinetic data for the $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ -catalyzed decomposition of hydrogen peroxide

Experiment number	$10^4[\text{Cu}_2]$ (M)	$[\text{H}_2\text{O}_2]$ (M)	$10^4 V_0$ (M s^{-1})	k_1 ($\text{M}^{-0.5} \text{s}^{-1}$)
1	4.28	0.17	1.27	0.037
2	8.56	0.17	2.52	0.052
3	12.9	0.17	2.96	0.050
4	17.1	0.17	3.48	0.051
5	25.7	0.17	4.22	0.050
6	17.1	0.13	3.02	0.055
7	17.1	0.20	5.50	0.066
8	17.1	0.23	6.15	0.063
9	17.1	0.27	5.67	0.052
10	17.1	0.33	7.39	0.053

Table 4
Kinetic data for the $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ -catalyzed decomposition of hydrogen peroxide

Experiment number	$10^4[\text{Cu}_2]$ (M)	$[\text{H}_2\text{O}_2]$ (M)	$10^4 V_0$ (M s^{-1})	k_2 ($\text{M}^{-1} \text{s}^{-1}$)
1	3.32	0.17	0.32	0.59
2	8.33	0.17	0.90	0.65
3	12.5	0.17	1.18	0.57
4	16.7	0.17	1.76	0.63
5	25.0	0.17	2.62	0.63
6	16.7	0.10	1.00	0.60
7	16.7	0.23	2.65	0.68

$\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ have such activity. The catalase-like activity of the complexes $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ and $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ was examined in acetonitrile at 20 °C. The amount of residual hydrogen peroxide (measured by iodometric titration) was compared with the amounts of dioxygen formed (as calculated by volumetry) and found to satisfy the stoichiometry implied by (Eq. (1)):



The observed initial rates for these complexes are compiled in Table 3. When the catalase activity was studied, complex $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ was the more reactive. The estimated initial rates (under same conditions) were $V_0 = 2.96 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$, and $V_0 = 1.18 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$, respectively, to the $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ and $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ compounds. Therefore, the $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$ complex is almost three-fold more reactive than compound $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$, toward hydrogen peroxide. In order to determine the rate dependence on the various reactants disproportionation runs were performed at different substrate and catalyst concentrations (Tables 3 and 4). While the influence of catalyst concentration on the kinetics exhibited a different profile (Fig. 2), both complexes showed a pseudo-first order dependence on the concentration of hydrogen peroxide (Fig. 3), resulted in the following experimental rate equations (Eqs. (2) and (3)):

$$\frac{d[\text{O}_2]}{dt} = k_{\text{phga}}[\text{Cu}_2(\text{bpy})_2(\text{phga})_4]^{0.5}[\text{H}_2\text{O}_2] \quad (2)$$

$$\frac{d[\text{O}_2]}{dt} = k_{\text{ba}}[\text{Cu}_2(\text{ba})_4(\text{bpy})_2][\text{H}_2\text{O}_2] \quad (3)$$

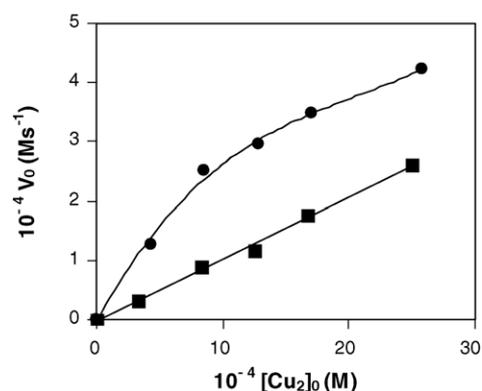


Fig. 2. Influence of the complex concentration on the initial rate of the decomposition of hydrogen peroxide, catalyzed by: $[\text{Cu}_2(\text{bpy})_2(\text{phga})_4]$ (●); and $[\text{Cu}_2(\text{ba})_4(\text{bpy})_2]$ (■); $[\text{H}_2\text{O}_2] = 0.17 \text{ M}$; in MeCN at 20 °C.

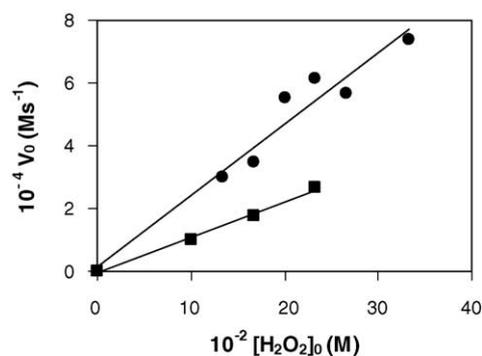
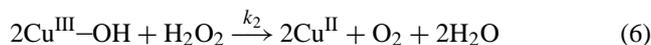
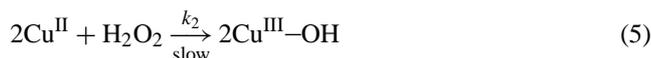


Fig. 3. Curves of the initial rate of the catalyzed decomposition of hydrogen peroxide as a function of hydrogen peroxide concentration. $[\text{Cu}_2(\text{bpy})_2(\text{phga})_4]$ (●) as the catalyst ($17.10 \times 10^{-4} \text{ M}$); and $[\text{Cu}_2(\text{ba})_4(\text{bpy})_2]$ (■) as the catalyst ($16.70 \times 10^{-4} \text{ M}$); in MeCN at 20 °C.

From Eqs. (2) and (3) a mean value of the kinetic constants k_{phga} of $0.05 \text{ M}^{-1/2} \text{ s}^{-1}$ and k_{ba} of $0.62 \text{ M}^{-1} \text{ s}^{-1}$, at 20°C were obtained, respectively. These values matches with the most active Mn- and Cu-catalase model systems [20,44,45].

On the basis of the kinetic data the following mechanism for the catalytic reaction steps can be proposed (Eqs. (4)–(6)):



The dimeric copper carboxylate complexes dissociate to monomeric copper species (Eq. (4)) in a fast pre-equilibrium. The monomeric complexes react then in the rate-determining step with H_2O_2 undergoing oxidative addition of the peroxide bond to Cu^{II} giving (hydroxo)copper(III) complexes. These react then in a fast consecutive step with further H_2O_2 ending-up in mononuclear Cu(II), dioxygen, and H_2O . The oxidative addition of H_2O_2 on Cu(II) may be supported by a similar reaction of CuCl with dibenzoyl peroxide giving a stable Cu(III) complex of the structure of $\text{CuCl}(\text{PhCO}_2)_2(\text{py})_2$ [46]. In order to explain the difference in the concentration dependence of the overall rate equation on the two copper complexes we deduced the real rate expression for both catalytic processes. By applying steady-state treatment for $d[\text{Cu}^{\text{III}}]/dt = 0$ [47] in the case of $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$, rate equation (Eq. (7)) could be obtained.

$$\text{reaction rate}_{\text{phga}} = k_2[\text{H}_2\text{O}_2] \sqrt{\frac{2k_1[\text{Cu}_2]}{2k_{-1} + k_2[\text{H}_2\text{O}_2]}} \quad (7)$$

Now, if K_1 is very small (the pre-equilibrium lies mainly on the left side) the rate equation simplifies to Eq. (8), which

$$\text{reaction rate}_{\text{phga}} = k_2 K_1^{0.5} [\text{Cu}_2^{\text{II}}]^{0.5} [\text{H}_2\text{O}_2] \quad (8)$$

applies for the (ketocarboxylato)copper complex $\text{Cu}_2(\text{bpy})_2(\text{phga})_4$. If K_1 is big Eq. (9) can be obtained, which satisfies the kinetic data obtained for the (benzoato)copper complex catalyzed reaction. That means that the complex $\text{Cu}_2(\text{ba})_4(\text{bpy})_2$ is extensively dissociated and the mononuclear species is mainly present during the catalytic process. The structure of monomeric $\text{Cu}(\text{ba})_2(\text{bpy})$ complex with H_2O coligand is known [48], showing that in case of the well-coordinating ligands such as water present the dimer easily dissociates into the monomeric form.

$$\text{reaction rate}_{\text{ba}} = k_2[\text{Cu}^{\text{II}}][\text{H}_2\text{O}_2] \quad (9)$$

4. Conclusion

We report here a new catalytic method for the disproportionation of H_2O_2 into H_2O and O_2 by using copper(II)

carboxylate complexes as catalyst. The simplicity of the system, easy preparation of the catalysts and applicability make copper carboxylate catalyzed decomposition of H_2O_2 an attractive, environmentally acceptable tool. On the basis of kinetic data a plausible mechanism is proposed assuming (hydroxo)copper(III) species as intermediate. However, evidence for its presence is still missing. It is also noteworthy that (ketocarboxylato)copper complexes have a much higher activity than the corresponding (carboxylato)copper complexes. The rate dependence on the catalyst suggests that the benzoato copper complex is mainly in the monomeric form, while that of the ketocarboxylato complex exist in the dimeric form with a small K_1 value.

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