Two novel Cu(II) complexes: Synthesis, structure and application in C–H bond activation

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A B S T R A C T

Two novel Cu(II) complexes $[Cu_2(H_2L)_2(3,5\text{-pyridinedicarboxylic})(H_2O)]\cdot2NO_3\cdot2H_2O$ (**1**) and $[Cu(2,2'\text{-bipy})(ad)_{1.5}]\cdot H_3O\cdot2H_2O$ (**2**) (H_2L = 2,6-di-(5-methyl-1H-pyrazol-3-yl)pyridine, H_2ad = hexane diacid) were synthesized and characterized by elemental analysis and IR spectra. Their catalytic performances were studied in cyclohexane (Cy) oxidation at mild condition. The total TON (turn over number) value raised from 61 to 271 with the addition of HNO_3 promoted by complex **2**, while from 0 to 143 by adding the mixture of HCl and lactic acid by complex **1**.

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1. Introduction

As the main components of natural gas and oil, hydrocarbons, particularly alkanes, are abundant and relatively cheap potential carbon raw materials. Their C–H bond(s) can be converted to C–OH or C=O functional groups, leading to the production of more valuable products for fine chemical synthesis [1–5], such as the cyclohexane (Cy) oxidation. The products of cyclohexanol (CyOH) and cyclohexanone (CyO) (the mixture is commonly known as the KA oil) are important intermediates for the synthesis of caprolactam and adipic acid [6]. Hence, searching efficient catalyst for such reactions becomes a hot topic since the high inertness of saturated hydrocarbons under mild conditions impedes their broad synthetic use [7–11].

Many transition metal complexes, especially Cu(II) complexes, were found to have high catalytic activities in alkanes oxidation [12–14]. $[Cu_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\mu\text{-buta})_2(MeOH)(H_2O)]_2$ (Hpz: pyrazole; Hbuta: butanoic acid) and $[Cu_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\mu\text{-EtCOO})_2(\text{EtOH})]_n$ were used for Cy oxidation by Nicola in the presence of HNO_3 and H_2O_2. The total yields of main products are 30% and 31%, respectively [15]. Nicola and his co-workers synthesized a Cu(II) complex $[Cu_3(\mu_3\text{-OH})(\mu\text{-pz})_3(EtCOO)_2(H_2O)]$ and found that it showed a good catalytic activity (the yield of main product is 28%) in Cy oxidation by H_2O_2 with HNO_3 as additive in MeCN [16]. Nesterov and co-workers found that the Cu(II) complex

$[Cu_2Co_2Fe_2(\mu\text{-dea})_6(NCS)_4(MeOH)_2]\cdot3.2H_2O$ (H_2dea: diethanolamine) had potential catalytic activity for Cy and cyclopentane oxidation with H_2O_2 in the presence of HNO_3, and the yield is 45% and 36%, respectively [17]. Kirillov reported that the total yield is 39% when $[Cu_4(\mu_4\text{-O})(\mu_3\text{-tea})_4(\mu_3\text{-BOH})_4][BF_4]_2$ (H_3tea: triethanolamine) acted as catalyst with H_2O_2 and HNO_3 in Cy oxidation [18].

Kirillov and his co-workers found that the kind of acid additives is also a key factor that significantly affects the reaction rate. The reaction proceeds extremely rapidly in the presence of HCl, being one order faster than those promoted by other acids (H_2SO_4, HNO_3, and TFA), and allowing to achieves the remarkably high turnover frequencies (TOFs) of ca. 600 h^{-1} [19]. But, in most cases, HNO_3 is needed as additive in such reactions [20–23]. Otherwise, no CyO and CyOH can be formed [24]. However, the use of HNO_3 leads serious drawbacks. First of all, there are certain amounts of NO and NO_2 released, which results in many environmental problems [25]. Secondly, HNO_3 as a strong oxidizing acid generally made the products be oxidized excessively. Finally, safety problems were hidden in the using of the process since HNO_3 is extremely corrosive. Recently, people try to find mild and environmental friendly acids to replace HNO_3 in such reactions. Pokutsa [26] use oxalic acid as additive in the Cy oxidation which catalyzed by VO(acac)$_2$, the total TON value reached to 944.

Herein, we designed and synthesized two novel Cu(II) complexes:$[Cu_2(H_2L)_2(3,5\text{-pyridinedicarboxylic})(H_2O)]\cdot2NO_3\cdot2H_2O$ (**1**) and $[Cu(2,2'\text{-bipy})(ad)_{1.5}]\cdot H_3O\cdot2H_2O$(ad = hexane diacid) (**2**). Their catalytic activities in Cy oxidation with H_2O_2 as the oxidant have been studied in detail. The effect of acid additives, especially a mild

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natural organic acid: lactic acid, is also being discussed. In addition, a possible reaction mechanism was proposed.

2. Experimental

2.1. Reagents and instruments

All chemicals purchased were of analytical grade and were used without further purification. H_2L were synthesized according to the literature method [27–29]. IR spectra were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer with pressed KBr pellets in the range 200–4000 cm^{-1}. A 30% aqueous solution of H_2O_2 was used as primary oxidant for catalytic reaction. The products were determined and analyzed by GC-9790 series gas chromatograph (Zhejiang Fuli Instrument Co. Ltd.) equipped with a FID detector and a capillary column. Nitrogen was used as the carrier gas.

2.2. Synthesis of complexes

Synthesis of complex 1: A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.1 mmol, 0.0242 g), H_2L (0.1 mmol, 0.0238 g) in methanol (10 mL) and water (2 mL) was stirred for 3–4 h. A few drops of 3,5-pyridinedicarboxylic acid (0.3 mmol, 0.0501 g) in 3 mL methanol was added with continuous stirring. The blue solution was stirred for 3 h before being sealed in a 25 mL Teflon-lined stainless-steel vessel under autogenous pressure and heated at 100 °C for 3 days, then cooled to 60 °C at 10 °C/3 h and further to room temperature slowly. Some blue crystals suitable for X-ray diffraction were obtained after leaving the dark-blue mother solution (filtering off the solid impurity) at room temperature for several days, Yield: 82.95% (based on Cu). *Anal.* Calc. for $C_{33}H_{35}N_{13}O_{13}Cu_2$ (948.82): C, 41.77; H, 3.70; N, 4.43. Found: C, 41.82; H, 3.67; N, 4.41. IR data (KBr, cm^{-1}):3441, 3058, 2930, 1622, 1574, 1466, 1380, 1291, 1016, 736, 587.

Synthesis of complex 2: $Cu(CH_3COO)_2 \cdot H_2O$ (0.0200 g, 0.1 mmol) in 5 mL water was added dropwise to a mixed methanol (10 mL) solution of 2,2′-dipyridyl (0.0156 g, 0.1 mmol) and hexane diacid (0.0146 g, 0.1 mmol). The blue solution was stirring for 3 h to get a dark green transparent solution. After filtration, placing the dark-green mother solution at room temperature for about 6 days, some dark blue crystals suitable for X-ray diffraction were obtained. Yield: 80.48% (based on Cu). *Anal.* Calc. for $C_{19}H_{26}N_2O_9Cu$ (490.98): C, 46.48; H, 5.31; N, 5.71. Found: C, 46.47; H, 5.27; N, 5.68%. IR data (KBr, cm^{-1}): 3527, 3085, 2950, 1681, 1555, 1417, 1310, 1223, 1037, 703, 558.

2.3. X-ray crystallographic determination

Suitable single crystals of the complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) and a ω scan mode. All absorption corrections were performed using the SADABS program [30]. Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. The crystallographic data and experimental details for data collection, as well as structure refinements, are given in Table 1. The drawings were made with the Diamond program. All calculations were performed using the SHELX-97 program [31].

2.4. Experimental for catalytic oxidation

The oxidation reactions were carried out under air condition (atmospheric pressure) in Schlenk tubes. In a typical experiment, 0.001 mmol of the catalysts (complex 1 or 2) was dissolved in 3.00 mL MeCN. Then the required amounts of H_2O_2 and desired

Table 1
Crystallographic data and structure refinement for complexes 1 and 2.

Complexes	1	2
Formula	$C_{33}H_{35}N_{13}O_{13}Cu_2$	$C_{19}H_{27}N_2O_9Cu$
M (g mol^{-1})	948.82	490.98
Crystal system	orthorhombic	triclinic
Space group	$Pna2(1)$	$P\bar{1}$
a (Å)	14.436(4)	9.6255(5)
b (Å)	13.104(3)	9.9447(5)
c (Å)	20.762(5)	12.7880(7)
α (°)	90	70.9180(10)
β (°)	90	73.7140(10)
γ (°)	90	75.6450(10)
V ($Å^3$)	3927.4(17)	1093.82(10)
Z	4	2
D_{calc} (Mg m^{-3})	1.605	1.491
Crystal size (mm)	$0.20 \times 0.16 \times 0.11$	$0.20 \times 0.15 \times 0.12$
$F(000)$	1944	512
μ (Mo Kα) (cm^{-1})	1.165	1.051
Reflections collected	1.84–28.34	2.20–24.99
Independent reflections($I > 2\sigma(I)$)	23 529	5514
Parameters	7667	3818
$\Delta(\rho)$ (e $Å^{-3}$)	520	280
Goodness-of-fit	0.780, –0.642	0.458, –0.420
R_1[a]	0.915	1.084
wR_2[a]	0.0374 (0.0427)[b]	0.0297 (0.0317)[b]

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$. [$F_o > 4(F_o)$].
[b] Based on all data.

acid were added according to this order. At last, a certain amount of Cy (or CyOH) was added into the solution to make the Cy (or CyOH)/catalyst molar ratio equals to 15 000:1. The reaction solution was stirred for 6 h at 50 °C.

For the products analysis, 0.03 g of methylbenzene (internal standard) and 1.5 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (0.2 μL) was taken from the organic phase and analyzed by a GC equipped with a capillary column and a flame ionization detector by the internal standard method. TON is moles of products (CyOH or CyO)/mole of catalyst.

3. Results and discussion

3.1. Synthesis

The two copper complexes have been successfully prepared for the first time (Scheme 1). To meet the coordinated conditions of ligands with copper atoms together in the reaction system, herein we have done our endeavor to search for the optimistic reaction conditions. For complex 1, the single crystals which suitable for X-ray diffraction could not be obtained when ethanol–water used as solvent at 120 °C until changing the solvent into the mixture of methanol and water and readjusting the ratio of them. The results show that the kind of solvent is an important reaction parameter of the crystal growing in the reaction system. Similarly, the crystals of complex 2 could not be obtained when the mixtured solution was heated at 120, 80, or 60 °C, but room temperature. It is worth to note that different starting materials of Cu(II) were used in the synthesis process of complexes 1 and 2. Exhausted experiments show that $Cu(NO_3)_2 \cdot 3H_2O$ is good reactant to prepare complexes 1 and 2, while $Cu(CH_3COO)_2 \cdot H_2O$ is only suitable for complex 2.

3.2. IR spectra

The IR spectra data of the complexes 1 and 2 are listed in Table 2. For the two complexes, the broad absorption bands in the region of 3257–3467 cm^{-1} were assigned to v(O–H) of the coordinated or