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# Synthesis, Structural Features, and Catalytic Activity of an Iron(II) 3D Coordination Polymer Driven by an Ether-Bridged Pyridine-Dicarboxylate

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**Abstract:** New iron(II) three-dimensional coordination polymer (3D CP),  $[Fe(\mu_3-Hcpna)_2]_n$  (1), was assembled under hydrothermal conditions from 5-(4'-carboxyphenoxy)nicotinic acid (H<sub>2</sub>cpna) as a trifunctional organic N,O-building block. This stable microcrystalline CP was characterized by standard methods for coordination compounds in the solid state (infrared spectroscopy, elemental analysis, thermogravimetric analysis, powder and single-crystal X-ray diffraction). Structure and topology of 1 were examined and permitted an identification of a 3,6-connected framework of the **rtl** topological type. In addition, compound 1 acts as effective catalyst precursor for oxidative functionalization of alkanes (propane and cyclic C<sub>5</sub>–C<sub>8</sub> alkanes) under homogeneous catalysis conditions, namely for the oxidation of saturated hydrocarbons with H<sub>2</sub>O<sub>2</sub>/H<sup>+</sup> system to produce ketones and alcohols, and for alkane carboxylation with CO/H<sub>2</sub>O/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system to obtain carboxylic acids. The influence of an acid promoter and substrate scope (propane and cyclic C<sub>5</sub>–C<sub>8</sub> alkanes) were investigated.

**Keywords:** metal-organic frameworks; coordination polymers; iron; hydrothermal synthesis; crystal engineering; C-H functionalization; homogeneous catalysis; cycloalkanes; propane; oxidation; carboxylation

## 1. Introduction

Coordination polymers (CPs) are now very popular compounds because of their highly diverse and unusual structures and interesting applications in various areas, which range from separation and sorption of gases [1–3] to luminescent [4,5] and catalytic materials [6–8], as well as molecular magnets [9,10] and sensors [11,12]. CPs are typically built from metal nodes and organic ligands such as polycarboxylic acids that act as spacers and/or linkers. Assembly and functional properties of CPs are usually affected by a diversity of parameters such as conditions of the synthesis, coordination preferences of metal nodes, as well as types of organic linkers or spacers [13–19].

The use of polycarboxylic acid ligands that combine different functional groups represents an interesting research direction for designing new types of coordination polymers or metal-organic frameworks (MOFs) [20–22]. Following our continuous interest in exploring new or poorly studied



multicarboxylic acids for the design of CPs [23–30], in this work we selected a trifunctional nicotinic acid derivative, 5-(4'-carboxyphenoxy)nicotinic acid (H<sub>2</sub>cpna) as a main building block. Selection of H<sub>2</sub>cpna can be justified by the following points. (1) This carboxylic acid can potentially act as a trifunctional ligand containing one phenyl and one pyridine ring which are connected by a gyrating *O*-ether functionality. (2) There are three different functional group classes (i.e., *N*-pyridyl, –COOH, *O*-ether) in H<sub>2</sub>cpna and six possible coordination sites. (3) H<sub>2</sub>cpna is still barely investigated for synthesis of CPs or MOFs. In fact, a search of the Cambridge Structural Database shows that there are only several examples of Zn, Cu, Ni, Co, Mn, Cd, and Pb coordination polymers assembled from H<sub>2</sub>cpna; some of them revealed interesting catalytic [8], sensing [11], gas sorption [21], luminescent [11,27], and magnetic [27] properties. Notable examples include a 2D Co(II) CP [Co( $\mu_3$ -cpna)(phen)(H<sub>2</sub>O)]<sub>n</sub>·nH<sub>2</sub>O {phen, 1,10-phenanthroline} applied as a heterogeneous catalyst for alcohol oxidation [8], a Tb<sup>3+</sup>-doped 3D Cu(II) MOF [Cu( $\mu_3$ -cpna)<sub>2</sub>]<sub>n</sub> used as a luminescent probe for sensing H<sub>2</sub>S [11], and a 2D porous framework [Cu( $\mu_3$ -cpna)(Me<sub>2</sub>NH)]<sub>n</sub>·nDMF·nH<sub>2</sub>O {DMF, dimethylformamide} with remarkable CO<sub>2</sub> sorption behavior in addition to single-crystal to single-crystal transformation features [21]. Despite these examples, iron derivatives of H<sub>2</sub>cpna remain virtually unknown.

Apart from this point, the selection of iron as a metal to construct a new coordination polymer is explained by its availability and high coordination versatility, as well as interesting redox chemistry that might be important for applications in catalysis. Thus, iron(II) sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) was explored as a low-cost and water-soluble iron(II) precursor for the hydrothermal synthesis of an H<sub>2</sub>cpna-derived compound. On the other hand, the hydrothermal synthetic conditions were used to aid the crystallization of a product as single crystals in addition to other advantages such as use of water as green reaction medium and no need for work-up to purify and isolate the product [26].

In this study, we describe a hydrothermal generation, characterization, crystal structure, topological interpretation, thermal stability, as well as catalytic behavior of a new iron(II) coordination polymer assembled from 5-(4'-carboxyphenoxy)nicotinic acid. The obtained product  $[Fe(\mu_3-Hcpna)_2]_n$  (1) is the first Fe coordination compound assembled from H<sub>2</sub>cpna. Besides, it also acts an efficient catalyst precursor for the oxidative functionalization of different saturated hydrocarbons under homogeneous conditions.

## 2. Experimental

#### 2.1. Materials and Physical Measurements

Analytical reagent grade chemicals were applied. H<sub>2</sub>cpna was acquired from a commercial supplier (Jinan Henghua Sci. & Tec. Co., Ltd, http://www.chemhh.com, catalogue code: 120511H-1B, purity 98%, CAS: 1777822-70-4). Elemental C, H, N analysis was run on an Elementar Vario EL elemental analyzer. Infrared (IR) spectra were obtained on a Bruker EQUINOX 55 spectrometer (KBr disks). TGA (thermogravimetric analysis) was carried out on a LINSEIS STA PT1600 thermal analyzer (N<sub>2</sub> atmosphere, 10 °C/min heating rate). PXRD (powder X-ray diffraction) pattern was obtained on a Rigaku-Dmax 2400 diffractometer (Cu-K $\alpha$  radiation;  $\lambda$  = 1.54060 Å). UV-Vis absorption spectra were determined on a Cary 5000 UV-vis-NIR spectrophotometer. For catalytic tests, GC (gas chromatography) analyses were carried out using an Agilent Technologies 7820A series gas chromatograph (FID: flame ionization detector; carrier gas: He; capillary column: BP20/SGE).

## 2.2. Synthesis of $[Fe(\mu_3-Hcpna)_2]_n$ (1)

 $FeSO_4$ ·7H<sub>2</sub>O (0.15 mmol, 41.7 mg), H<sub>2</sub>cpna (0.3 mmol, 77.7 mg), NaOH (0.3 mmol, 12.0 mg), and water (10 mL) were combined in a Teflon-lined stainless-steel reactor (25 mL volume) and stirred for 15 min at ambient temperature. The reactor was then sealed, heated for 3 days at 160 °C, and gradually cooled (10 °C/h rate) to ambient temperature. Yellow crystals (blocks) were manually isolated, washed with bidistilled water, and then air-dried to furnish compound **1**. Yield: 55% (on the bases of H<sub>2</sub>cpna). Calcd for C<sub>26</sub>H<sub>16</sub>FeN<sub>2</sub>O<sub>10</sub>: C 54.57, H 2.82, N 4.90%. Found: C 54.79, H 2.80, N 4.93%. IR (KBr, cm<sup>-1</sup>):

1646 s, 1605 m, 1579 m, 1511 w, 1455 w, 1398 s, 1304 m, 1273 s, 1242 w, 1206 m, 1164 m, 1112 w, 1050 w, 1014 w, 962 w, 895 w, 848 w, 785 w, 713 w, 693 w, 604 w, 547 w.

#### 2.3. X-ray Crystallography

For 1, single-crystal X-ray data were collected using a Bruker APEX-II CCD diffractometer with a graphite-monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å, Bruker Corporation, Billerica, MA, USA). Semiempirical absorption corrections were performed with SADABS software (Bruker AXS, version 5.624, Madison, Wisconsin, USA). Structure of 1 was determined by direct methods, followed by a refinement (full-matrix least-squares on  $F^2$ ) with SHELXS-97/SHELXL-97 [31,32]. Apart from H atoms, all other types of atoms underwent an anisotropic refinement (full-matrix least-squares on  $F^2$ ). Hydrogen atoms (with an exception of COOH group) were positioned in calculated sites having fixed isotropic thermal parameters. These were considered in structure factor calculations at the final stage of full-matrix least-squares refinement. For COOH group, H atom of was found using difference maps, followed by its restriction to be at its parent oxygen atom. Crystal parameters for 1 are summarized in Table 1. Topological description of metal-organic net in 1 was performed following the concept of underlying (simplified) network [33]. This net was built [33] by reducing  $\mu_3$ -Hcpna<sup>-</sup> blocks to respective centroids, while their connections with iron(II) nodes were maintained [34]. CCDC-1906984 for 1 contains the supplementary crystallographic data.

Compound	1		
Chemical formula	C <sub>26</sub> H <sub>16</sub> FeN <sub>2</sub> O <sub>10</sub>		
Molecular weight	572.26		
Crystal system	Monoclinic		
Space group	$P2_1/n$		
a/Å	9.4673(7)		
b/Å	9.2170(6)		
c/Å	14.0358(9)		
α/ (°)	90		
<i>β</i> /(°)	108.079(8)		
γ/ (°)	90		
$V/Å^3$	1164.30(15)		
Z	2		
F(000)	584		
Crystal size/mm	$0.27 \times 0.25 \times 0.23$		
heta Range for data collection	3.770-25.049		
Limiting indices	$-9 \le h \le 11, -10 \le k \le 10, -16 \le l \le 10$		
Reflections collected/unique (R <sub>int</sub> )	4273/2053 (0.0558)		
$D_{\rm c}/({\rm Mg}\cdot{\rm cm}^{-3})$	1.632		
$\mu/\mathrm{mm}^{-1}$	0.715		
Data/restraints/parameters	2053/0/179		
Goodness-of-fit on $F^2$	1.029		
Final <i>R</i> indices $[(I \ge 2\sigma(I))] R_1$ , w $R_2$	0.0502, 0.0890		
$R$ indices (all data) $R_1$ , w $R_2$	0.0895, 0.1084		
Largest diff. peak and hole/( $e \cdot Å^{-3}$ )	0.329 and -0.376		

 Table 1. Crystal structure parameters for coordination polymer 1.

#### 2.4. Catalytic Oxidation of Cyclic Alkanes

The reactions were carried out in glass reactors (50 mL volume, thermostated at 50 °C, and equipped with a reflux condenser) under aerobic conditions and constant magnetic stirring; acetonitrile was used as solvent and added up to 2.5 mL of the total volume of the reaction mixture. Typical reaction procedure: catalyst precursor **1** (0.005 mmol) was suspended in CH<sub>3</sub>CN and then an acid promoter (0.015–0.1 mmol) and a gas chromatography (GC) internal standard (CH<sub>3</sub>NO<sub>2</sub>, 250  $\mu$ L) were introduced. The oxidation reaction began on addition of cycloalkane (1 mmol) and H<sub>2</sub>O<sub>2</sub> (5 mmol, 50%)

in water) and its progress was followed by taking small aliquots of the reaction mixture at different periods of time. Before GC analysis (internal standard method), each aliquot was treated with a small amount of solid triphenylphosphine that is necessary to reduce cycloalkyl hydroperoxides (primary products in the oxidation of cycloalkanes) and remaining hydrogen peroxide; the product yields are based on the GC data after the treatment with PPh<sub>3</sub>. Blank tests were performed and showed that the oxidation of cycloalkanes does not occur in the absence of Fe catalyst.

#### 2.5. Catalytic Oxidation of Propane

The following reagents were combined in a stainless-steel reactor (20.0 mL total volume): catalyst precursor **1** (0.005 mmol), solvent CH<sub>3</sub>CN (up to 2.5 mL of total volume of the reaction mixture), acid promoter (PCA, 0.015 mmol or TFA, 0.1 mmol), CH<sub>3</sub>NO<sub>2</sub> (GC internal standard, 250  $\mu$ L), and H<sub>2</sub>O<sub>2</sub> (5 mmol, 50% in water). The reactor was then sealed, pressurized with C<sub>3</sub>H<sub>8</sub> (1 atm) and heated at 50 °C for 4 h under magnetic stirring. After cooling the reactor, it was degassed and the samples of the reaction mixtures were analyzed by GC (internal standard method). Before the analysis, the samples were treated with PPh<sub>3</sub>. Blank tests disclosed that the oxidation of propane does not occur in the absence of Fe catalyst.

## 2.6. Catalytic Carboxylation of Alkanes

Typical procedure: catalyst precursor 1 (0.01 mmol), CH<sub>3</sub>CN (4.0 mL), H<sub>2</sub>O (2.0 mL), cycloalkane substrate (1.0 mmol), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.50 mmol) were combined in a stainless-steel reactor (20.0 mL total volume). It was sealed and flushed three times with carbon monoxide to remove air and then pressurized with CO (20 atm). For carboxylation of C<sub>3</sub>H<sub>8</sub>, the reactor was first flushed and pressurized with the substrate (1 atm) and then CO was added. The reactor was heated at 50 °C for 4 h under magnetic stirring. After cooling the reactor, it was degassed and the reaction mixture was transferred to a glass flask. Diethyl ether (9.0 mL) and GC internal standard (cycloheptanone, 45  $\mu$ L) were added (cyclohexanone was used as a GC standard in cycloheptane carboxylation). The obtained mixture was stirred for 10 min and then the aliquots were withdrawn from organic layer and analyzed by GC (internal standard method).

#### 3. Results and Discussion

#### 3.1. Synthesis and Characterization

The hydrothermal synthesis (at 160 °C for 3 days) using a mixture in water of iron(II) sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), H<sub>2</sub>cpna (5-(4'-carboxyphenoxy)nicotinic acid) as a trifunctional organic block, and sodium hydroxide as a base resulted in a 3D coordination polymer formulated as  $[Fe(\mu_3-Hcpna)_2]_n$  (1). The molar ratio between FeSO<sub>4</sub>.7H<sub>2</sub>O, H<sub>2</sub>cpna, NaOH, and H<sub>2</sub>O was 1:2:2:3700, and the pH value of the initial reaction mixture was in the 4–5 range. The compound 1 was isolated in a good yield as a crystalline solid (including single crystals of X-ray quality) and characterized by conventional techniques, which also include a single-crystal X-ray diffraction. Product 1 is insoluble in any solvent and maintains its stability in e.g. CH<sub>3</sub>CN/H<sub>2</sub>O medium at 60 °C, as confirmed by powder X-ray diffraction (Figure S4, Supplementary Materials). In the IR spectrum of compound 1 (Figure S3, Supplementary Materials), the most characteristic, broad and intense bands of the carboxylate groups appear at 1605 and 1398 cm<sup>-1</sup> and correspond to  $v_{as}(COO)$  and  $v_{s}(COO)$  vibrations, respectively. Apart from these broad bands, there are also several minor shoulders or neighboring  $\nu$ (COO/COOH) bands centered at 1455, 1398, and 1304 cm<sup>-1</sup>. For H<sub>2</sub>cpna, the strongest vibrations of carboxylic acid groups are observed at 1676 and 1305 cm<sup>-1</sup> (Figure S2, Supplementary Materials). Different position of the main band maxima in  $\mathbf{1}$  and  $\mathbf{H}_2$  cpna indicates the coordination of carboxylic acid ligand to iron(II) centers in 1, as further supported by elemental and thermogravimetric analyses along with the PXRD and single-crystal X-ray diffraction data.

## 3.2. Description of Structural and Topological Features

Product **1** possesses a 3D coordination polymer structure (Figure 1). Its asymmetric unit bears one Fe(II) atom (with a half occupancy) and one  $\mu_3$ -Hcpna<sup>-</sup> block. The six-coordinate Fe1 atom displays the distorted {FeN<sub>2</sub>O<sub>4</sub>} octahedral environment (Figure 1a and Figure S1). It is completed by two nitrogen and four carboxylate oxygen donors coming from six  $\mu_3$ -Hcpna<sup>-</sup> moieties. The Fe–O [2.075(3)–2.183(3) Å] and Fe–N [2.152(3) Å] distances are typical for a present type of Fe(II) coordination compounds [35,36]. The Hcpna<sup>-</sup> ligand acts as a  $\mu_3$ -*N*,*O*<sub>2</sub>-spacer (Scheme 1) with the COOH and COO<sup>-</sup> groups adopting monodentate modes. The Hcpna<sup>-</sup> block is considerably bent showing a dihedral angle of 87.94° between benzene and pyridyl functionalities, while a C–O<sub>ether</sub>–C angle is 117.97°. The  $\mu_3$ -*N*,*O*<sub>2</sub>-Hcpna<sup>-</sup> blocks multiply link neighboring Fe(II) nodes to form a 3D CP structure (Figure 1b,c). Compound **1** shows no porosity, as confirmed by calculating an effective free volume of the crystal volume by PLATON; its unit cell contains no residual solvent accessible voids.



**Figure 1.** Different structural representations of **1**. (a) Connectivity and coordination sphere of the Fe1 center; hydrogen atoms are not shown with an exception of H in COOH. Symmetry operators: i = -x + 1, -y + 1, -z; ii = x, y, z - 1; iii = -x + 1, -y + 1, -z + 1; iv = -x + 1/2, y + 1/2, -z + 1/2; v = x + 1/2, -y + 1/2, z - 1/2. (b,c) Three-dimensional metal-organic network along the *a* and *c* axis, respectively. (d) Topological view of a 3D coordination polymer displaying a 3,6-connected binodal underlying net of the **rtl** (rutile) topological type. View along the *c* axis; colors: centroids of 3-connected  $\mu_3$ -Hcpna<sup>-</sup> nodes (gray), 6-connected Fe1 nodes (orange balls).



Scheme 1. The coordination mode of Hcpna<sup>-</sup> block in 1.

To better understand such intricate 3D coordination polymer structures, topological classification was carried out. Topologically, the 3D underlying net in **1** (Figure 1d) is constructed from 6-connected Fe1 and 3-connected  $\mu_3$ -Hcpna<sup>-</sup> nodes, thus disclosing a 3,6-connected binodal net of the **rtl** (rutile) topological type. This net can be described with a  $(4 \cdot 6^2)_2 (4^2 \cdot 6^{10} \cdot 8^3)$  point symbol, in which the  $(4 \cdot 6^2)$  and  $(4^2 \cdot 6^{10} \cdot 8^3)$  notations are those of  $\mu_3$ -Hcpna<sup>-</sup> and Fe1 nodes, respectively.

## 3.3. TGA and PXRD

The stability and thermal behavior of CP **1** were investigated by running TGA (thermogravimetric analysis, Figure 2a) under nitrogen atmosphere in the 20–800 °C range of temperatures. CP **1** does not contain solvent of crystallization or H<sub>2</sub>O ligands and remains stable until 248 °C; further increase of temperature leads to the decomposition of the sample.



**Figure 2.** Thermogravimetric analysis (TGA) curve (**a**) and powder X-ray diffraction (PXRD) patterns (**b**) of **1**.

Besides, crystalline sample of CP 1 was studied by PXRD (powder X-ray diffraction analysis) and an experimental PXRD pattern of the bulk product is shown in Figure 2b. Comparison of the experimental pattern with that calculated from single-crystal X-ray diffraction confirms the presence of a single pure phase in the sample of 1. Moreover, elemental analysis corroborates an analytical purity of this coordination polymer.

#### 3.4. Catalytic Functionalization of Alkanes

Following our continuous interest in developing different metal-complex-catalysts and protocols for oxidative functionalization of saturated hydrocarbons under mild conditions [37–40], we explored a catalytic potential of **1** in oxidation of cyclic  $C_5$ – $C_8$  alkanes and propane to give the respective alcohol and ketone products. Cyclohexane was investigated as a model substrate and the reactions were performed at 50 °C with hydrogen peroxide as oxidant (50% in water) in CH<sub>3</sub>CN/H<sub>2</sub>O medium and using a slight amount of acid as a promoter.

The use of  $CH_3CN$  as a solvent is important for solubilization of an alkane and catalyst since the oxidation reactions practically do not undergo in only  $H_2O$  as a solvent. Selection of acetonitrile can be justified by the following factors: (i) miscibility of  $CH_3CN$  with  $H_2O$  and aqueous  $H_2O_2$ , (ii) sufficient solubility of alkanes in  $CH_3CN$ , (iii) good stability of acetonitrile in the reaction medium, and (iv) good prior results for oxidative functionalization of alkanes obtained when using  $CH_3CN$  as a solvent of choice [37–44].

It should be mentioned that the CP **1** is not intact during catalytic experiments and acts as a precursor of homogeneous catalytically active species. These form upon dissolution of **1** in the presence of oxidant and acid promoter. Cyclohexane oxidation to cyclohexanone and cyclohexanol does not occur without catalyst **1** (Figure 3), either in the absence or in the presence of acid promoter. In the presence of **1**, the oxidation of  $C_6H_{12}$  undergoes very slowly unless an acid promoter is added (Figure 3). However, an addition of TFA (trifluoroacetic acid; commonly used for promoting the activity of various Cu and Fe based catalytic systems [37–39]) causes a drastic acceleration of reaction rate and higher quantity of products generated (8% yield after 90 min of the reaction). The presence of PCA (2-pyrazinecarboxylic acid) in a very low amount (molar ratio PCA:**1** = 3:1) results in higher catalytic activity (15% total product yield after 90 min, Figure 3). It should be mentioned that PCA is a recognized and powerful promoter in different metal-catalyzed oxidations of hydrocarbons [41].



**Figure 3.** Influence of acid promoter on  $C_6H_{12}$  oxidation by hydrogen peroxide to a mixture of cyclohexanone and cyclohexanol (total product yield vs. reaction time) catalysed by **1**. Conditions: **1** (0.005 mmol),  $C_6H_{12}$  (1.0 mmol),  $H_2O_2$  (5.0 mmol, 50% in  $H_2O$ ), 2-pyrazinecarboxylic acid (PCA, 0.015 mmol) or trifluoroacetic acid (TFA, 0.05–0.10 mmol), CH<sub>3</sub>CN (solvent added up to 2.5 mL of total volume of the reaction), 50 °C. Blank tests without catalyst precursor **1** (curve: no catalyst; in the presence of TFA, 0.1 mmol) or acid promoter (curve: no acid, in the presence of **1**; 0.005 mmol) are given for comparison.

Other cycloalkanes also undergo oxidation with  $H_2O_2$  in the presence of catalyst 1 and PCA promoter (Figure 4). In particular, the oxidation of cycloheptane (to cycloheptanol and cycloheptanone) and cyclooctane (to cyclooctanol and cyclooctanone) proceeds more efficiently (total product yield up to 22%) than that of cyclohexane and cyclopentane.



**Figure 4.** Substrate scope in oxidation of cyclic  $C_5-C_8$  alkanes with  $H_2O_2$  to corresponding ketones and alcohols (total product yield vs. reaction time) catalyzed by **1**. Conditions: **1** (0.005 mmol),  $C_5H_{10}-C_8H_{16}$  (1.0 mmol),  $H_2O_2$  (50% in  $H_2O$ , 5.0 mmol), PCA (0.015 mmol), CH<sub>3</sub>CN (solvent added up to 2.5 mL of total volume of the reaction), 50 °C.

Upon addition of PCA, compound **1** also efficiently catalyses the oxidation of a light gaseous alkane such as propane (Table 2) to give a mixture of *i*-propanol, acetone, *n*-propanol, and propanal with a total product yield of 22% (based on  $C_3H_8$ ). However, if TFA is used as a promoter, the reaction is less efficient (total product yield of 7.3%). It should be highlighted that the product yield of up to 22% (based on propane) obtained herein is remarkable, especially if taking into account a very high inertness of this gaseous hydrocarbon along with rather mild conditions applied for running the oxidation reaction [37–41].

Catalyst	Product Yield (%) <sup>b</sup>				
	<i>i</i> -Propanol	Acetone	n-Propanol	Propanal	Total
1/PCA	6.1	11.3	3.0	1.6	22.0
1/TFA	2.1	2.3	1.5	1.4	7.3

**Table 2.** Mild oxidation of propane with  $H_2O_2$  catalyzed by 1<sup> a</sup>.

<sup>a</sup> Conditions: **1** (0.005 mmol), PCA (0.015 mmol) or TFA (0.1 mmol),  $C_3H_8$  (1 atm, 0.7 mmol),  $H_2O_2$  (50% in  $H_2O_2$  5.0 mmol),  $CH_3CN$  (solvent added up to 2.5 mL of total volume of the reaction), 50 °C, 4 h in a stainless-steel reactor (20 mL capacity). <sup>b</sup>.Yields based on  $C_3H_8$  substrate: (moles of products/moles of  $C_3H_8$ ) × 100%.

In addition, compound **1** was evaluated as catalyst precursor in the carboxylation of cyclic  $C_n$  (n = 5–8) alkanes and propane in the presence of CO (carbonyl source), H<sub>2</sub>O (hydroxyl source) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (oxidant and radical initiator) [42–44]. These carboxylations undergo in H<sub>2</sub>O/CH<sub>3</sub>CN at 60 °C and result in generation of the respective  $C_{n+1}$  carboxylic acids (main products, Table 3). The oxidation  $C_n$  products (e.g., cyclic ketones and alcohols) are also formed due to competing oxidation reactions, especially when using cyloheptane and cyclooctane as substrates.

Substrate	Yield (%) <sup>b</sup>				
	Cycloalkane-Carboxylic Acid	Cyclic Ketone	Cyclic alcohol	Total	
Cyclopentane	13.9	3.4	1.7	19.0	
Cyclohexane	20.9	1.1	0.6	22.6	
Cycloheptane	9.2	6.5	2.5	18.2	
Cyclooctane	4.8	7.8	5.9	18.5	

Table 3. Single-pot carboxylation of cycloalkanes catalyzed by 1<sup>a</sup>.

<sup>a</sup> Conditions: 1 (0.01 mmol),  $C_5H_{10}-C_8H_{16}$  (1 mmol), CO (20 atm),  $K_2S_2O_8$  (1.5 mmol), CH<sub>3</sub>CN (4 mL)/H<sub>2</sub>O (2 mL), 60 °C, 4 h in a stainless-steel reactor (20 mL capacity). <sup>b</sup> Yields based on cycloalkane substrate: (moles of products/moles of cycloalkane) × 100%.

Among the cycloalkane substrates tested, more elevated yields of carboxylic acid products are obtained in cyclohexane carboxylation (21% of  $C_6H_{11}COOH$ ) and cyclopentane carboxylation (14%  $C_5H_9COOH$ ). Interestingly, the transformations of cycloheptane and cyclooctane result in lower yields of carboxylic acids (5–9%) but higher yields of ketones and alcohols, while the total yields of products in all systems are in the 18–23% range. The carboxylation of propane generates *i*-butyric acid (13.6% yield; main product) and *n*-butyric acid (3.8% yield; minor product) owing to two types of C atoms in  $C_3H_8$  molecule.

Taking into account the mechanistic considerations from the related oxidation and carboxylation processes catalysed by various coordination compounds [37–44], we can propose the free radical pathways for the reactions studied in the present work (Figure 5). In both alkane oxidation and carboxylation reactions, compound 1 acts as a precursor of homogeneous Fe-cpna species when reacting with oxidant and/or acid promoter; these species are formed upon partial protonation of some carboxylate groups and ligand decoordination. In fact, the catalyst precursor facilitates the formation of active oxidizing species (i.e., hydroxyl radicals from  $H_2O_2$  in alkane oxidation or sulfate radical anions from  $K_2S_2O_8$  in alkane carboxylation) and eventually participates in other mechanistic steps (Figure 5).



Figure 5. Simplified mechanism for oxidation and carboxylation of alkanes.

Hence, in alkane oxidation, the substrate molecules (RH) are activated by HO<sup>•</sup> to produce alkyl radicals (R<sup>•</sup>). These are coupled with dioxygen (present in air or generated from hydrogen peroxide) to furnish alkyl peroxo radicals (ROO<sup>•</sup>) that are further converted, via ROO<sup>-</sup>, to alkyl hydroperoxides (ROOH) as intermediate products. In fact, the formation of ROOH was corroborated by performing the duplicate GC tests for selected reaction mixtures (Shul'pin's method), namely by analyzing them after and before treating with PPh<sub>3</sub> [45,46]. ROOH are not very stable under the reaction conditions and undergo decomposition (can also be iron-catalyzed) to generate ROH and R'=O as final alkane oxidation products [37,42].

In carboxylation of saturated hydrocarbons, RH react with  $SO_4^-$  as active oxidizing species to form R<sup>•</sup>. Alkyl radicals are carboxylated by CO to give acyl radicals (RCO<sup>•</sup>) and then acyl cations (RCO<sup>+</sup>). These are prone to undergo hydrolysis by H<sub>2</sub>O to generate carboxylic acids (RCOOH) as principal products (Figure 5). Competitive oxidation of R<sup>•</sup> to form ROH and R'=O as by-products is also observed in the present type of carboxylation processes [42–44].

## 4. Conclusions

This work described a facile hydrothermal generation and full characterization of the new Fe(II) 3D coordination polymer derived from 5-(4'-carboxyphenoxy)nicotinic acid (H<sub>2</sub>cpna) as a multifunctional organic building block. The obtained product **1** reveals the first structurally characterized Fe(II) compound assembled from H<sub>2</sub>cpna [47].

The structure and topology of this iron 3D CP were established and discussed, revealing a 3,6-connected underlying network of the **rtl** topological type. Compound **1** also functions as active catalyst precursor for the homogeneous oxidation and carboxylation of propane and cycloalkanes under mild conditions, leading to up to 23% yields of products (based on alkane substrate). These values of yields are excellent considering a particular inertness of saturated hydrocarbons (especially propane) and mild conditions of the reactions studied [48–50]. For example, a related industrial process of cyclohexane oxidation to cyclohexanone and cyclohexanol (DuPont process with a homogeneous Co naphthenate catalyst) shows only 5–10% substrate conversions [51,52] and proceeds under harsher reaction conditions (10–15 atm pressure, 150 °C, air oxidant).

Although the present homogeneous catalytic systems derived from 1 still cannot be recycled, we believe future research aiming at trapping 1 or its soluble derivatives on solid supports might result in the development of reusable heterogeneous catalysts for alkane functionalization. Furthermore, further studies on exploring H<sub>2</sub>cpna and related multifunctional building blocks for the hydrothermal design of new metal-organic architectures will be continued in our laboratories.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4352/9/7/369/s1, Figure S1: ellipsoid plot of **1**, Figures S2 and S3: FT-IR spectra, Figure S4: additional PXRD patterns and discussion, Figures S5 and S6: UV-vis spectra, Tables S1 and S2: selected bonding and H-bonding parameters for **1**.

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