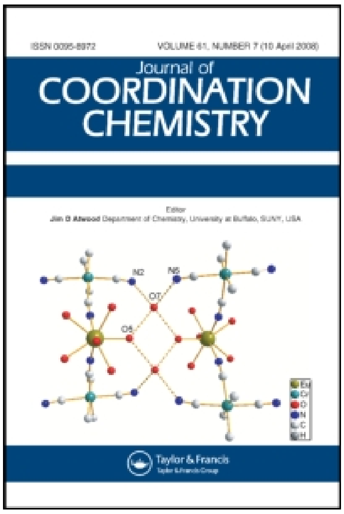

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The influence of pH on coordination of phthalate to copper(II)

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The influence of pH on coordination of phthalate to copper(II)

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Two phthalate structures and a copper coordination polymer, $(phth)_2(H_2O)_2$ (**1**), $(phth)_2(H_2O)_3$ (**2**), and $Cu(phth)_2(H_2O)_2$ (**3**) [phth = phthalate], have been synthesized hydrothermally. The complexes were studied by single crystal X-ray analysis, elemental analysis, IR spectra and TG-DTG. Single crystal X-ray analysis reveals that **1** belongs to the orthorhombic system, space group *Pca*2(1), **2** is the monoclinic system, space group *C*2/*c* and **3** has four-coordinate Cu(II). The copper complex forms a one-dimensional zigzag chain via π–π stacking interaction of phthalates. Adjacent zigzag chains may be paired by supramolecular recognition and attraction through both π–π stacking and hydrogen bonding interactions into molecular zippers, further interlinked into a three-dimensional supramolecular network by these noncovalent interactions.

Keywords: Copper complex; Coordination polymer; pH value

1. Introduction

Interest has focused on crystal engineering of supramolecular architectures organized by coordinate covalent bonds or supramolecular contacts such as hydrogen bonding and π–π interactions [1–3]. Self-assembly of these architectures is influenced by ligands [4], molar ratio of the reagents [5], the pH of the solution [3f, 6] and steric requirement of the counterions [7]. Further exploration of synthetic strategies is a continuing challenge to extend the knowledge of relevant structural types and establish proper synthetic strategies for desirable supramolecular species.

Magnetic and spectroscopic properties of phthalate metal compounds have been studied [8], but few single-crystal structures have been reported [9]. Here we report synthesis, characterization and solid state structure as well as thermal stability.

To investigate supramolecular interactions of phthalates, $(phth)_2(H_2O)_2$, $(phth)_2(H_2O)_3$, and $Cu(phth)_2(H_2O)_2$ [phth = phthalate] were synthesized by reaction of potassium hydrogen phthalate, and $Cu(NO_3)_2 \cdot 3H_2O$ with HCl or KOH at different pH's. In **1** and **2**, phth is not coordinated to Cu(II) but have strong hydrogen bonds with lattice water contributing to the packing of complexes.

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2. Experimental

2.1. *Synthesis of (phth)$_2$(H$_2$O)$_2$ (1)*

All reagents were of AR grade and used without further purification. Potassium hydrogen phthalate (0.2040 g, 1 mmol) was dissolved in 10 mL EtOH/H_2O (v : v = 1 : 1), and then the resultant solution was added to 10 mL of double-distilled water containing $Cu(NO_3)_2 \cdot 3H_2O$ (0.2426 g, 1 mmol). The mixed solution was acidified with 1 M HCl to pH = 3. The resulting solution was heated at 373 K for 96 h. After cooling to room temperature, transparent crystals were obtained in a yield of 31.23%. Elemental analysis calculated for **1**: C, 52.13; H, 4.34%. Found: C, 51.61; H, 4.23%.

2.2. *Synthesis of (phth)$_2$(H$_2$O)$_3$ (2)*

The procedure was similar to that for **1** except that the mixed solution was basified with 1 M NaOH to pH = 6 (45% yield). Anal. Calcd for **2**: C, 49.72; H, 4.66%. Found: C, 49.31; H, 4.56%.

2.3. *Synthesis of Cu(phth)$_2$(H$_2$O)$_2$ (3)*

The procedure was similar to that for **1** except that the mixed solution was basified with 1 M KOH to pH = 8 (34% yield). Anal. Calcd for **3**: C, 44.67; H, 3.26%. Found: C, 43.31; H, 3.16%.

2.4. *Structure determinations of 1, 2 and 3*

X-ray crystallography. Suitable single crystals of **1**, **2** and **3** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 291 K. An empirical absorption correction was applied using the SADABS program [10]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELX-97 program package [11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of PyBIm were generated geometrically; no attempts were made to locate the hydrogen atoms of water and hydrosulfate. The crystallography details for the structure determinations of **1**, **2** and **3** are presented in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Syntheses and characterization*

Attempts to obtain products by reaction of potassium hydrogen phthalate and $Cu(NO_3)_2 \cdot 3H_2O$ in solution failed. When refluxed in acetonitrile-water solution for

Table 1. Crystal data and structure refinement parameters for **1**–**3**.

	1	**2**	**3**
Formula	$C_{16}H_{16}O_{10}$	$C_8H_9O_{5.50}$	$C_{16}H_{14}CuO_{10}$
Crystal size (mm^3)	$0.20 \times 0.18 \times 0.17$	$0.20 \times 0.13 \times 0.15$	$0.35 \times 0.18 \times 0.19$
Molecular mass	368.29	193.15	438
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pca2(1)*	*C2/c*	*P2(1)/c*
a (Å)	9.821(2)	13.585(3)	8.3895(17)
b (Å)	13.358(3)	21.219(4)	14.441(3)
c (Å)	6.5290(13)	6.8659(14)	7.0992(14)
α (°)	90	90	90
β (°)	90	113.65(3)	112.14(3)
γ (°)	90	90	90
V (Å^3)	856.6(3)	812.9(6)	796.7(3)
Z	2	8	2
T (K)	291(2)	291(2)	291(2)
D_{calc} (g cm^{-3})	1.428	1.415	1.792
$F(000)$	384	808	438
Reflections collected	2742	2824	2640
Independent reflections	1509	1598	1422
Data/restraints/parameters	1509/3/135	1598/2/136	1422/2/137
Goodness-of-fit on F^2	1.084	1.060	1.100
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0658$ $wR_2 = 0.1702$	$R_1 = 0.0791$ $wR_2 = 0.2378$	$R_1 = 0.0376$ $wR_2 = 0.0998$
R indices (all data)	$R_1 = 0.0682$ $wR_2 = 0.1767$	$R_1 = 0.0902$ $wR_2 = 0.2479$	$R_1 = 0.0401$ $wR_2 = 0.1080$

$R_1 = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

Complex **1**			
O(1)–C(7)	1.223(5)	C(2)–C(1)–C(6)	119.1(3)
O(2)–C(7)	1.317(4)	C(2)–C(1)–C(7)	120.6(3)
O(3)–C(8)	1.262(5)	C(6)–C(1)–C(7)	120.2(3)
O(4)–C(8)	1.252(5)	C(3)–C(2)–C(1)	121.4(4)
C(1)–C(2)	1.393(5)	C(5)–C(4)–C(3)	120.4(4)
C(1)–C(6)	1.404(5)	C(4)–C(5)–C(6)	120.6(4)
Complex **2**			
O(1)–C(7)	1.287(4)	C(2)–C(1)–C(6)	119.5(3)
O(2)–C(7)	1.238(4)	C(2)–C(1)–C(7)	117.7(3)
O(3)–C(8)	1.316(4)	C(6)–C(1)–C(7)	122.8(3)
O(4)–C(8)	1.229(4)	C(3)–C(2)–C(1)	120.6(3)
C(1)–C(2)	1.391(5)	C(5)–C(4)–C(3)	120.0(3)
C(1)–C(6)	1.403(5)	C(4)–C(5)–C(6)	120.8(3)
C(1)–C(7)	1.513(5)	C(5)–C(6)–C(1)	119.0(3)
C(2)–C(3)	1.384(5)	C(5)–C(6)–C(8)	121.0(3)
C(6)–C(8)	1.483(5)	O(2)–C(7)–O(1)	125.2(3)
Complex **3**			
Cu(1)–O(1)#1	1.9362(19)	O(1)#1–Cu(1)–O(1)	180.0
Cu(1)–O(1)	1.9362(19)	O(1)#1–Cu(1)–O(5)#1	89.10(9)
Cu(1)–O(5)#1	1.944(2)	O(1)–Cu(1)–O(5)#1	90.90(9)
Cu(1)–O(5)	1.944(2)	O(1)#1–Cu(1)–O(5)	90.90(9)
O(1)–C(7)	1.255(3)	O(1)–Cu(1)–O(5)	89.10(9)
O(3)–C(8)	1.304(3)	C(7)–O(1)–Cu(1)	109.78(17)
C(6)–C(8)	1.517(4)	C(3)–C(4)–C(5)	120.0(3)

Symmetry transformations used to generate equivalent atoms: $1 - x + 2$, $-y$, $-z + 2$.

a day, the white powder gave crystals of very poor quality. Hydrothermal synthesis was adopted in the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with potassium hydrogen phthalate in water under varied conditions. When the mixture was acidified with 1M HCl to pH = 3, both complexes **1** and **2** could be obtained as an inseparable mixture with **2** in poor quality. When the pH was increased to 6 and 8, **2** and **3** could be obtained.

3.2. *IR spectra*

In **1** and **2**, the $1728\,cm^{-1}$ absorption is assigned to $\nu(C{=}O)$ of carboxyl. In addition, a strong and broad band at $3340\,cm^{-1}$ was assigned to $\nu(OH)$ with hydrogen bonds or water molecules. Bands at 1595 and $1376\,cm^{-1}$ of **3** are related to $\nu_{asym}(OCO^-)$ and $\nu_{sym}(OCO^-)$, respectively.

3.3. *TG-DTG properties*

The TGA diagrams show the compounds have different stability in the 25–900°C range. Complex **1** exhibits loss of one lattice water between 60–90°C (6.6% weight loss observed; 4.9% calculated). In contrast, **2** exhibits loss of three waters between 500–600°C (9.1% weight loss observed; 9.3% calculated). Complex **3** has three main mass loss stages. The first at 8.04% starts at 373.5 K and ends at 424.5 K while reaching its highest rate at 419.4 K, attributed to the loss of coordination H_2O (calcd. 8.37%). The second mass loss (39.92%) starts at 424.5 K and ends at 508.3 K, reaching its highest rate at 486.6 K. It is inferred that one phthalate (35.35%) is lost at this stage. The last obvious weight loss stage with 33.99% starts at 508.3 K and ends at 706.8 K, reaching its highest rate at 582.6 K, attributed to the loss of another phthalate (calcd. 35.35%). The residue is 18.05% of the total mass.

3.4. *Crystal structures*

Compound **1** crystallizes in the chiral space group Pca2(1). The single crystal X-ray structure analysis reveals that **1** is a one-dimensional chain with all phenyls of the phthalate on the outside of the chain. Adjacent phthalate rings in the chain are not parallel with dihedral angles of 47.36°. The O–H groups of phthalate form strong hydrogen bonds with oxygen atoms of lattice water (figure 1) [O(2)–H(2E) $\cdots$ O(3)#1 2.590(4) Å, ∠O(2)–H(2E) $\cdots$ O(3)#1 = 120(6)°, O(4)–H(4E) $\cdots$ O(5)#2 3.027(4) Å, ∠O(4)–H(4E) $\cdots$ O(5)#2 = 131(4)°, O(5)–H(5F) $\cdots$ O(3)#3 2.895(3), ∠O(5)–H(5F) $\cdots$ O(3)#3 = 136(4)° O(5)–H(5E) $\cdots$ O(4)#4 2.834(4), ∠O(5)–H(5E) $\cdots$ O(4)#4 = 164(6)°. Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, y, $z-1/2$, #2 $x+1/2$, $-y$, z, #3 $-x+1/2$, y, $z-1/2$, #4 $-x+1/2$, y, $z+1/2$] (table 3).

Compound **2** crystallizes as a racemic twin in space group C2/c as one-dimensional columnar chains. Adjacent phthalate rings in the chain are almost coplanar with dihedral angle of 4.169°. O–H groups of phthalate form strong hydrogen bonds with lattice water (figure 2) [O(1)–H(1B) $\cdots$ O(1)#1 2.475(5), ∠O(1)–H(1B) $\cdots$ O(1)#1 175.2°, O(5)–H(5F) $\cdots$ O(1)#2 2.793(4), ∠O(5)–H(5F) $\cdots$ O(1)#2 167(4)°, O(5)–H(5E) $\cdots$ O(2)#3 2.779(4), ∠O(5)–H(5E) $\cdots$ O(2)#3 174(5)°, O(3)–H(3B) $\cdots$ O(5) 2.604(4),

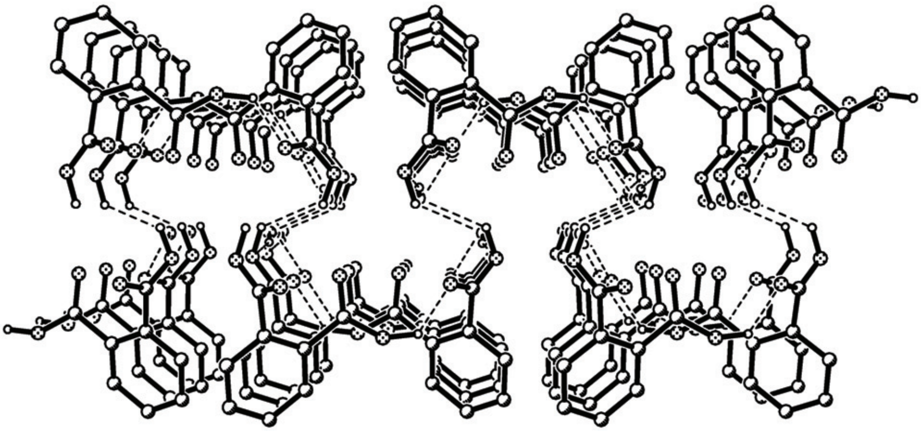


Figure 1. The H-bonded network for **1**.

Table 3. Hydrogen-bonding geometry and close contacts (Å, °) for **1**–**3**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	d(D–H···A)
Complex **1**[a]				
O(2)–H(2E)···O(3)#1	1.18(9)	1.79(8)	2.590(4)	120(6)
O(4)–H(4E)···O(5)#2	1.05(5)	2.24(5)	.027(4)	131(4)
O(5)–H(5F)···O(3)#3	0.87(2)	2.20(4)	2.895(3)	136(4)
O(5)–H(5E)···O(4)#4	0.84(2)	2.02(3)	2.834(4)	164(6)
Complex **2**[b]				
O(1)–H(1B)···O(1)#1	0.82	1.66	2.475(5)	175.2
O(5)–H(5F)···O(1)#2	0.96(5)	1.84(5)	2.793(4)	167(4)
O(5)–H(5E)···O(2)#3	0.95(2)	1.83(2)	2.779(4)	174(5)
O(3)–H(3B)···O(5)	0.82	1.79	2.604(4)	172.5
O(6)–H(6F)···O(4)	0.86(2)	2.02(2)	2.876(3)	170(6)
Complex **3**[c]				
O(5)–H(5F)···O(4)#2	0.86(2)	1.82(2)	2.667(3)	166(5)
O(5)–H(5E)···O(3)#3	0.871(19)	.94(2)	2.794(3)	166(4)
O(3)–H(3E)···O(2)	0.84(5)	1.57(5)	2.404(3)	172(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, y, $z-1/2$, #2 $x+1/2$, $-y$, z, #3 $-x+1/2$, y, $z-1/2$, #4 $-x+1/2$, y, $z+1/2$.

[b] Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z+1/2$, #2 x, $-y+1$, $z-1/2$, #3 x, $-y+1$, $z+1/2$.

[c] Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y$, $-z+2$, #2 $-x+2$, $y-1/2$, $-z+3/2$, #3 x, $-y+1/2$, $z-1/2$.

∠O(3)–H(3B)···O(5) 172.5°, O(6)–H(6F)···O(4) 2.876(3), ∠O(6)–H(6F)···O(4) 170(6)°]. Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z+1/2$, #2 x, $-y+1$, $z-1/2$, #3 x, $-y+1$, $z+1/2$ (table 3).

Structure analysis reveals that Cu(II) in **3** is four-coordinate (figure 3). The asymmetric unit consists of one Cu(II), one phthalate anion and one H_2O molecule. The Cu(II) is located at the distorted square (O(1)#1–Cu(1)–O(1) 180.00(11)°, ∠O(1)–Cu(1)–O(5)#1 90.91(10)°, ∠O(1)#1–Cu(1)–O(5)#1 89.09(10)°, ∠C(7)–O(1)–Cu(1) 109.81(17)° and ∠O(5)#1–Cu(1)–O(5) 180.00(15)°) (table 3). Symmetry transformations: #1 $-x$, $-y$, $-z$.

The copper complex forms one-dimensional zigzag chains via π–π stacking of phthalate, face-to-face with the distance of 3.647 Å. A 3D network structure is formed

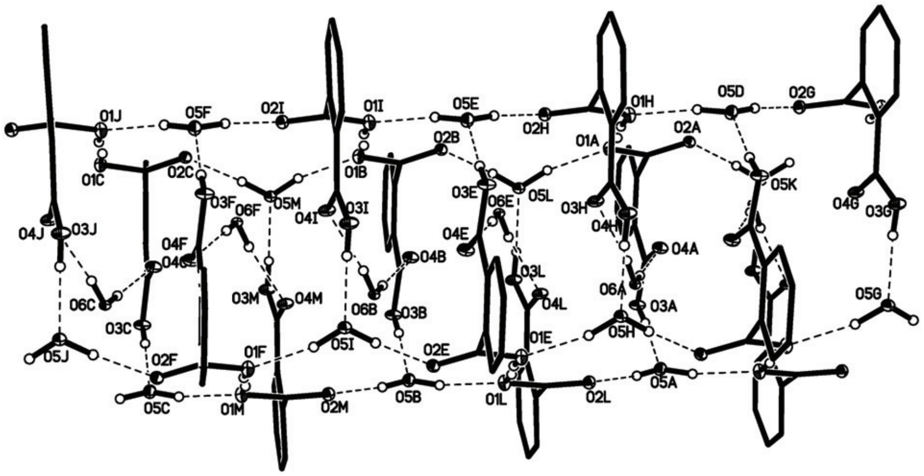


Figure 2. Extensive hydrogen-bonding of **2**.

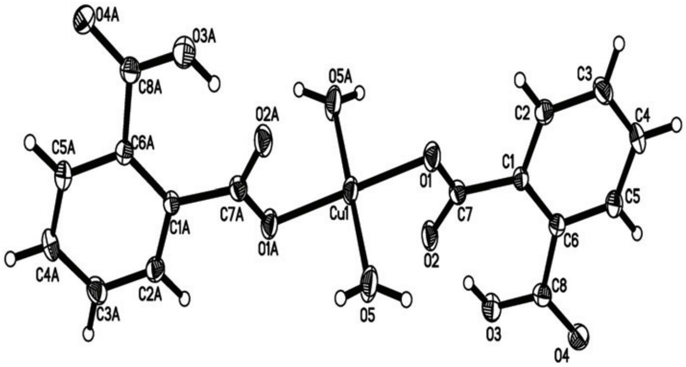


Figure 3. ORTEP plot of **3** with 30% probability ellipsoid.

by π–π stacking interaction of phthalate and hydrogen bonds, such as O(3)–H(3E) = 0.84(5) Å, H(3E) ··· O(2) = 1.57(5) Å, O(3) ··· O(2) = 2.404(3) Å, ∠O(3)–H(3E) ··· O(2) = 172(5)° of two phthalates coordinated to copper (figure 4). Another O–H ··· O hydrogen bond is between the water coordinated to copper and phthalate, involving H(5E) atom with O(3)#3 (O(5)–H(5E) = 0.871(19) Å, H(5E) ··· O(3)#3 = 1.94(2) Å, H (5E) ··· O(3)#3 = 2.794(3) Å, ∠O(5)–H(5A) ··· O(4A) = 166(4)°) and H(5F) atom bound to O(5) (O(5)–H(5F) = 0.86(2) Å, H(5F) ··· O(4)#2 = 1.82(2) Å, O(5) ··· O(4)#2 = 2.667(3) Å, ∠O(5)–H(5F) ··· O(4)#2 = 166(5)°). Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y$, $-z+2$, #2 $-x+2$, $y-1/2$, $-z+3/2$, #3 x, $-y+1/2$, $z-1/2$.

3.5. *Catalytic oxidation of cyclohexene properties (Compound 3)*

Oxidation of cyclohexene was carried out in acetone at room temperature under magnetic stirring in the presence of **3** as the catalyst using 30% H_2O_2. The reaction was

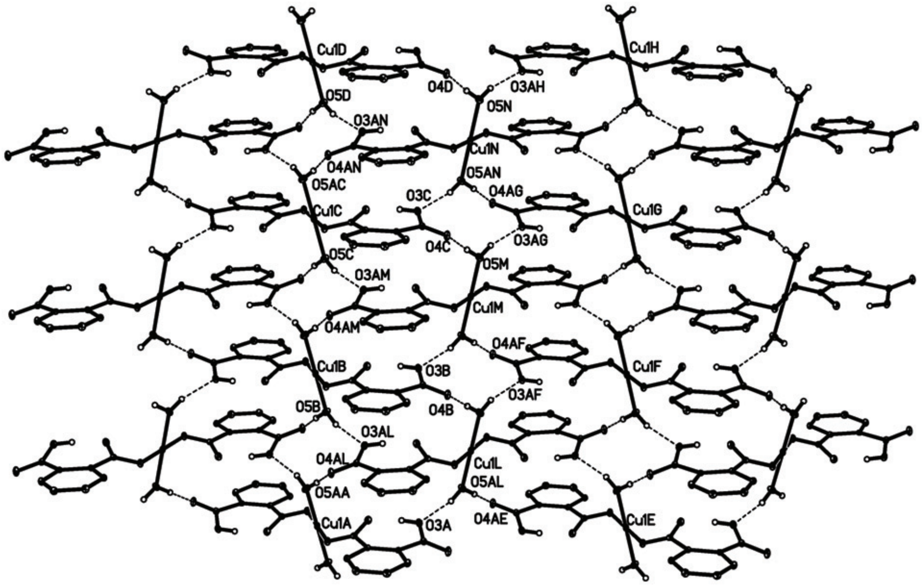
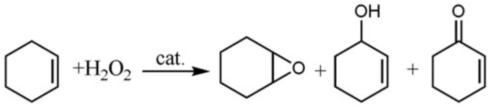


Figure 4. Hydrogen bonds of **3**.

monitored by GC analysis of solution samples taken periodically to determine the concentrations of the various oxidation products. In a typical experiment, 1 mL of hydrogen peroxide (30%) was added to the reaction mixture containing cyclohexene (1 mL) and catalyst (39 mg) in 1 mL acetone. The results, identified by GC-MS, are summarized in table 4. Distribution of products was strongly dependent on the ratio of $[C_6H_{10}]$ to $[H_2O_2]$. The largest specificity was obtained using **3** as catalyst and a concentration ratio of 1 : 10. Under these conditions the allylic hydrogen is more reactive than the C=C double bond, and the reaction proceeds to give 2-cyclohexen-1-one as the main product and



cyclohexene epoxide with the lowest yield (entry 1, table 4). In control experiments using cyclohexene under identical experimental conditions, but excluding metal complex, or in the presence of $Cu(NO_3)_2 \cdot 3H_2O$, did not give any oxidation products.

In summary, two phthalate compounds and a copper coordination polymer have been synthesized hydrothermally at different pH's. Complex **3** forms one-dimensional zigzag chains via π-π stacking of phthalate.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC: (**1**) 650137; (**2**) 650415; (**3**) 650136.

Table 4. Catalytic oxidation of cyclohexene with H_2O_2 for **3**.

Time	Ratio $C_6H_{10}:H_2O_2$	Alkene (%)	Epoxide (%)	Ketone (%)	Alcohol (%)
1 mL, 24 h	1 : 10	0.78	0.66	94.47	4.15
1 mL, 24 h	1 : 8	6.29	1.46	86.34	5.96
1 mL, 24 h	1 : 4	36.76	4.86	43.13	15.24
0.5 mL, 2 h	1 : 8	1.54	7.96	87.49	2.98
0.5 mL, 2 h	1 : 8	2.32	12.31	74.31	11.14

Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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