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# Calcium coordination compounds based on phenoxyacetic acids: Microwave synthesis, thermostability and influences on the crystal structures of chlorine substituent group on ligands

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Three calcium coordination compounds,  $[Ca(CPA)(H_2O)_4] \cdot (CPA)$ , **1**,  $[Ca(MCPA)_2(H_2O)_2] \cdot H_2O$ , **2**, and  $[Ca(TCPA)_2(H_2O)_3] \cdot 2H_2O$ , **3** [HCPA = 3-chlorophenoxyacetic acid, HMCPA = 2-methyl-4-chlorophenoxyacetic acid and HTCPA = 2,4,6-trichlorophenoxyacetic acid], have been synthesized by the microwave method with advantages that include shorter reaction times, lower-energy consumption, and higher product yield. The structures have been characterized by IR, elemental analysis, and single-crystal X-ray diffraction. Influences on the crystal structures by changing the number and position of chlorine substituent group in phenoxyacetic acid are discussed. Steric hindrance effects involving the Cl and an ability to form the O-H…Cl hydrogen bonds enrich the structure diversity. TG analysis reveals that the thermostability for the three compounds is **3>1>2**, which could be influenced by the existence of hydrogen-bonds (O-H…Cl and O-H…Q).

*Keywords*: Calcium coordination compounds; Microwave method; Crystal structure; Thermostability

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#### 1. Introduction

Calcium coordination compounds have drawn much more attention owing to valuable applications in tunable fluorescent indicators [1-3], ion sensing [4], homogeneous catalysts [5, 6] and metal-organic frameworks (MOFs) for selective adsorption of CO<sub>2</sub> and N<sub>2</sub> [7-9]. Ligands used to construct these coordination compounds are mainly focused on Schiff bases, protein, heterocyclic compounds and aromatic carboxylic acids [10-13]. Chlorophenoxyacetic acids are one of the most widely used aromatic carboxylic acid ligands with their own unique advantages. First, the carboxyl group can bond with metal through a variety of coordination modes [14]. Second, chlorophenoxyacetic acids possess flexibility owing to the presence of a -OCH<sub>2</sub>- spacer between the phenyl ring and carboxylate [15]. Third, the chlorine substituent on benzene ring is beneficial to the formation of O-H…Cl hydrogen-bonds. The three points above assist the self-assembly process, giving more chances for structure diversity. A number of coordination compounds based on chlorophenoxyacetic acids have been studied involving Li [16], Ag [17]. Co [18], Zn [19], Mn [20], Cd [21], Fe [22], Gd [23], La and Nd [24]. In these works, phenoxyalkanoic acids form coordination compounds with metal ions, however, only one case of calcium based on 2,4-dichlorophenoxyacetate has been reported [25]. Prompted by the above cases, three different chlorophenoxyacetic acids, HCPA, HMCPA and HTCPA, have been selected to construct calcium coordination compounds in this work. The synthesis used microwave synthesis, which has proven to be an effective method to obtain crystals [26]. Effect on the crystal structures by changing the number and position of chlorine substituents on ligands are also discussed. Although chlorine substituents do not coordinate to the metal, a steric hindrance effect and ability to form the O-H…Cl hydrogen-bond enriches the diversities of the structures. The relationship between thermostability and structure has also been studied. The order of thermostability is 3>1>2, which may be influenced by hydrogen-bonds.

#### 2. Experimental

#### 2.1. Materials and physical measurements

3-Chlorophenol, 4-chloro-2-methylphenol, 2,4,6-trichlorophenol and ethyl chloroacetate were purchased commercially from Aladdin Reagent Co. Ltd. (Shanghai, China). Microwave synthesis was performed using a CEM Discover SP single-mode microwave reactor. Elemental analyses (C and H) were performed on a Vario MACRO cube elemental analyzer. IR spectra were recorded on a BRUKER TENSOR 27 spectrophotometer from 400-4000 cm<sup>-1</sup> using the samples prepared as pellets with KBr. TG analyses were performed on a SHIMADZU TA-60ws from 25 to 1000 °C at a heating rate of 10 °C·min<sup>-1</sup> in N<sub>2</sub>.

#### 2.2. Synthesis of the ligands and coordination compounds

**2.2.1. Synthesis of HCPA, HMCPA and HTCPA.** The three ligands were prepared by microwave synthesis in the following route (scheme 1). A mixture of 3-chlorophenol (5 mmol) for **1**, 4-chloro-2-methylphenol (5 mmol) for **2** or 2,4,6-trichlorophenol (5 mmol) for **3**, ethyl chloroacetate (5 mmol), K<sub>2</sub>CO<sub>3</sub> (5 mmol), KI (1 mmol), PEG-600 (0.5 mmol) and DMF (2 mL) was irradiated in a microwave oven under 200 W for 4 min, then 5 mL of NaOH (2 M) was added and irradiated 5 min at 500 W. After cooling to room temperature, the resulting aqueous solution was acidified (pH = 6) by the addition of a 1 M HCl solution under vigorous stirring. Column chromatography provided three white solids. <sup>1</sup>H NMR (DMSO/TMS, 500 MHz, ppm): **HCPA** (Yield: 88%)  $\delta$  13.17 (s, 1H), 7.40 (t, *J* = 8.3 Hz, 1H), 7.14-7.07 (m, 2H), 7.02-6.97 (m, 1H), 4.83 (s, 2H), **HMCPA** (Yield: 86%)  $\delta$  13.04 (s, 1H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.15 (dt, *J* = 10.3, 5.1 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 4.70 (d, *J* = 12.1 Hz, 2H), 2.18 (s, 3H). **HTCPA** (Yield: 83%)  $\delta$  13.25 (s, 1H), 7.81 (s, 2H), 4.68 (s, 2H).



Scheme 1. Syntheses of **HCPA**: X<sub>2</sub>=Cl, **HMCPA**: X<sub>1</sub>=CH<sub>3</sub>, X<sub>3</sub>=Cl, **HTCPA**: X<sub>1</sub>=Cl, X<sub>3</sub>=Cl, X<sub>4</sub>=Cl.

#### 2.2.2. Syntheses of 1-3

2.2.2.1.  $[Ca(CPA)(H_2O)_4]$  (CPA), **1**. A mixture of **HCPA** (0.2 mmol), CaCl<sub>2</sub>·2H<sub>2</sub>O (0.1 mmol), NaOH (0.2 mmol) and deionized water (8 mL) was placed in a microwave reaction tube. The mixed solution was sealed and heated at 100 °C at 120 W in a microwave reactor for 1 h. Upon cooling to room temperature at 10 °C·h<sup>-1</sup>, colorless, block crystals suitable for X-ray diffraction were obtained (yield 82% based on Ca). Anal. calc. for C<sub>16</sub>H<sub>20</sub>CaCl<sub>2</sub>O<sub>10</sub>: C, 39.73; H, 4.14 %. Found: C, 39.71; H, 4.15 %. IR data (cm<sup>-1</sup>): v(O-H): 3409b; v(Ar-O-C): 1233m, 1098s, 1050s;  $v_{asym}$ (COO<sup>-</sup>): 1625s, 1569s;  $v_{sym}$ (COO<sup>-</sup>): 1476s, 1422s; v(-CH<sub>2</sub>-): 683m.

2.2.2.2.  $[Ca(MCPA)_2(H_2O)_2]$   $H_2O$ , 2. The procedure was similar to that of 1 except using **HMCPA** instead of **HCPA**. Colorless, hexagon bulk crystals for 2 were obtained with yield of 72% based on Ca. Anal. calc. for C<sub>18</sub>H<sub>22</sub>CaCl<sub>2</sub>O<sub>9</sub>: C, 43.78; H, 4.46 %. Found: C, 43.77; H, 4.45 %. IR data (cm<sup>-1</sup>): v(O-H): 3415b; v(Ar-O-C): 1229m, 1179s, 1071s;  $v_{asym}$ (COO<sup>-</sup>): 1487s, 1448s, 1422s; v(-CH<sub>2</sub>-): 722m.

2.2.2.3.  $[Ca(TCPA)_2(H_2O)_3]\Box H_2O$ , 3. The procedure was similar to that of 1 except using **HTCPA** instead of **HCPA**. Colorless, rod-like crystals for 3 were obtained with yield of 86% based on Ca. Anal. calc. for C<sub>16</sub>H<sub>18</sub>CaCl<sub>6</sub>O<sub>11</sub>: C, 30.04; H, 2.82 %. Found: C, 30.05; H, 2.81 %. IR data (cm<sup>-1</sup>): v(O-H): 3412b; v(Ar-O-C): 1257m, 1191s, 1081s, 1033;  $v_{asym}(COO^-)$ : 1630s, 1575s;  $v_{sym}(COO^-)$ : 1466s, 1422s;  $v(-CH_2-)$ : 724m.

#### 2.3. Single-crystal X-ray structure determinations

All crystallographic data were collected on a Bruker SMART CCD area-detector diffractometer at 298(2) K with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) in  $\omega$  scan mode, and the data reduction was performed using Bruker SAINT. The crystal structures were resolved by direct methods and refined with full-matrix least-squares refinement on  $F^2$  with anisotropic displacement parameters for non-H atoms using SHELXTL [27]. All non-hydrogen atoms and hydrogens were refined geometrically. Structural plots were generated with Diamond. A summary of crystallographic data for 1-3 is presented in table 1. Selected bond lengths and angles for 1-3 are given in table 2. Hydrogen bonding distances and angles for 1-3 are listed in table 3.

#### 3. Results and discussion

#### 3.1. Structural descriptions for 1-3

**3.1.1. Crystal structure of [Ca(CPA)(H<sub>2</sub>O)<sub>4</sub>] (CPA), 1.** Single-crystal X-ray diffraction analysis reveals that the crystal system and space group for 1 are triclinic and *P*-1, respectively. The asymmetric unit contains one Ca(II) centre, one coordinated CPA, four coordinated water molecules, and one lattice CPA. Each Ca(II) is coordinated by eight oxygens, of which three (O1A, O1 and O2WB) belong to CPA and the other five (O1W, O1WB, O2W, O3W and O4W) come from coordination water molecules. The coordination environment around Ca(II) is presented in figure 1(a) with atom numbering scheme. The eight-coordinate Ca(II) is in a distorted bicapped trigonal prism, where O1A, O2W and O3W form the top plane of the trigonal prism and the bottom plane is completed by O1, O1W and O1WB, while O4W and O2WB cap two quadrilateral faces formed by O1WB-O1-O1A-O3W and O1W-O2W-O3W-O1WB, respectively. The coordination mode of CPA in 1 is  $\mu_3$ - $\eta^2$ :  $\eta^1$ , which means one oxygen links two metal ions and the other oxygen connects one metal ion, so the carboxyl group coordinates to three ions. The carboxyl group of the CPA and coordination water connect neighboring Ca(II) ions to form a 1D linear chain with  $\{Ca_2(CPA)_2(H_2O)_2\}_n$  dimeric repeat units, which shows drum-like and tetragon configurations appearing alternately along the *b*-axis (figure 2(a)). An interesting structural feature for 1 is the formation of the 2D layer by hydrogen-bond interactions involving the lattice **CPA** molecules and coordinated water. Specifically, in the  $\{Ca_2(CPA)_2(H_2O)_2\}_n$  dimeric repeat units, hydrogen-bonds are formed between coordinated water and uncoordinated **CPA**, in which O1W, O2W, O3W and O4W donate hydrogens to oxygen of uncoordinated **CPA**. The uncoordinated **CPA** serves as a bidentate bridge to link coordinated water of neighboring chains. In this manner, parallel 1D chains (figure 2(b)) are involved in hydrogen-bond interactions to form a 2D layer (figure 2(c)) in the *ac* plane.

**3.1.2. Crystal structure of [Ca(MCPA)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O, 2. Coordination compound 2 crystallizes** in the monoclinic crystal system and P2(1)/c space group. The asymmetric unit consists of one Ca(II), two **MCPA** anions, two coordinated waters and one lattice water (figure 3(a)). Each Ca(II) is also eight coordinate by six carboxylate oxygens (O1, O1B, O2A, O2B, O4, O5) from **MCPA** ligands and two water molecules (O7, O8). Similar to **1**, the Ca(II) is also in a distorted bicapped trigonal prism, where O1B, O2B and O7 form the top plane of the trigonal prism and the bottom plane is completed by O8, O4 and O5, while O1 and O2A cap two quadrilateral faces formed by O2B-O4-O8-O7 and O1B-O5-O8-O7. Different from **1**, the MCPA ligands in **2** show two coordination modes:  $\mu_3$ - $\eta^2$ :  $\eta^2$  (figure 3(b)) and  $\mu_1$ - $\eta^1$ :  $\eta^1$  (figure 3(c)), respectively.

In **2**, the infinite 1D zigzag chain is formed through connection of the metal centers by carboxyl group oxygens of **MCPA** ligands, alternately arranged on both sides of the zigzag chain (figure 4(a)). The 2D layer (figure 4(b)) was formed by two kinds of hydrogen-bond interactions: 1) the hydrogen-bond between carboxyl group oxygen and lattice water and 2) the hydrogen-bond between oxygens of lattice water and hydrogens of coordinated water molecules.

**3.1.3. Crystal structure of [Ca(TCPA)**<sub>2</sub>(**H**<sub>2</sub>**O**)<sub>3</sub>]**·**2**H**<sub>2</sub>**O**, **3.** Single crystal X-ray diffraction analysis reveals that **3** crystallizes in the triclinic crystal system and *P*-1 space group. As shown

in figure 5(a), the asymmetric unit contains one crystallographically unique Ca(II), two **TCPA** anions, three coordinated waters and two lattice waters. The eight-coordinate Ca(II) exhibits a bicapped trigonal prism with top plane completed by O1W, O2B, O3, bottom plane completed by O6B, O5A, O3W, and two caps of O2W and O5 corresponding to the quadrilateral faces of O3-O3W-O6B-O1W and O2B-O5A-O3W-O3. From figure 6(a), the 1D metal-node-based chain with the unique feature of an eight-membered ring and chair-like configuration alternately along the *b*-axis is formed through the calcium connections linked by the ligands through coordination modes of  $\mu_2$ - $\eta^2$ :  $\eta^1$  in figure 5(b) and  $\mu_2$ - $\eta^1$ :  $\eta^1$  in figure 5(c).

As shown in figure 6, the 2D layer for 2 was formed by the hydrogen-bond (O-H…Cl and O-H…O) interactions involving **TCPA** ligands and coordinated water as well as lattice water. The lattice water can form hydrogen-bonds with the coordinated water (such as O2W-H2WA…O6W) and also hydrogen-bonds with the carboxylic oxygen (O5W-H5WA…O6), which is similar to 1 and 2. Lattice water molecules (O5W, O6W) can also donate two free hydrogens (H5WB, H6WB) to chlorine of **TCPA** (the two *o*-position chlorines), then form O5W-H5WB…Cl5 and O6W-H6WB…Cl3 hydrogen-bonds, which are not found in 1 and 2. The construction of 1D phenoxyacetic acid coordination compounds which are further extended into 2D layer assisted by O-H…Cl hydrogen-bond interactions remains scarce.

**3.1.4. Influences on crystal structures by changing number and position of chlorine substituent.** The number and position of the chlorine substituent in aromatic rings of **1-3** affect formation of O-H…Cl hydrogen-bonds. All three coordination compounds have intermolecular O-H…O hydrogen-bonds, however, only **3** has O-H…Cl hydrogen-bonds. As shown in figure 7, the distances between chlorine and the nearest oxygen are 6.93 Å for *m*-position substituted chlorine in **1** (figure 7(a)) and 5.62 Å for *p*-position substituted chlorine in **2** (figure 7(b)); both are too far to form the O-H…Cl hydrogen-bond. There are two *o*-position substituted chlorines in **3**, one has a distance of 2.59 Å with oxygen of lattice water (figure 7(c)).

#### 3.2. Thermogravimetric analysis of 1-3

Coordination compounds 1-3 have three general mass-loss steps (figure 8). The first mass-loss is for release of water molecules including all coordinated as well as lattice waters from 95.89-202.97 °C for 1, 64.64-141.40 °C for 2, and 89.97 -185.57 °C for 3. The experimental mass-losses (calculated mass loss) for 1-3 were 14.678% (14.898%), 10.47% (10.945%) and 14.563% (14.083%). The next two mass-losses correspond to continuous collapse of the frameworks, from 202.97 °C to 726.18 °C for 1, 141.40 °C to 571.83 °C for 2, and 185.57 °C to 789.12 °C for 3. The final residue could be assigned to CaO, with the experimental residue (calculated residue) of 11.771% (11.602%) for 1, 11.015% (11.367%) for 2, and 9.28% (8.775%) for 3. The final decomposition temperature is in the order 3>1>2(789.12 °C>726.18 °C>571.83 °C), which reveals the thermostability for the three compounds is also in the order 3>1>2. The results of TG coincide quite well with the structures. From the structural analysis above, we can clearly see that O-H…O hydrogen-bonds exist in all three title

compounds, but O-H…O hydrogen-bonds in **2** are more complex than **1**, so the thermostability of **1** is higher than **2**. For **3**, O-H…Cl hydrogen-bonds coexist with O-H…O hydrogen-bonds, resulting in the most stable structure among the three coordination compounds.

#### 4. Conclusion

Three new calcium coordination compounds based on phenoxyacetic acids were microwave synthesized and characterized (FI-IR, elemental analysis, single-crystal X-ray diffraction). All Ca(II) ions are coordinated by eight oxygens in distorted bicapped trigonal prism arrangements. The three compounds were very different in the extension of the 1D chain into the 2D layer. For 1, the 2D layered network was formed by the O-H…O hydrogen-bond interactions between the uncoordinated **CPA** and coordinated water. For **2**, the 2D layered network was formed by the O-H…O hydrogen and lattice water, or between oxygen of lattice water and hydrogen of coordinated water. For **3**, the 2D layered network was formed by O-H…O hydrogen-bonds together. Results of thermal

analysis proved the thermostability of the three compounds follows the order 3>1>2, which coincide well with the structures.

#### Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC-1401086, CCDC-1401090 and CCDC-1401091. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail:deposit@ccdc.cam.ac.uk).

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ecordination compounds	1	2	3
Empirical formula	$C_{16}H_{20}CaCl_2O_{10}$	C <sub>18</sub> H <sub>22</sub> CaCl <sub>2</sub> O <sub>9</sub>	$C_{16}H_{18}CaCl_6O_{11}$
Formula weight	483.30	493.34	639.08
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	P2(1)/c	P-1
a, Å	6.6460(10)	18.1509(15)	7.5532(11)
b, Å	7.3050(10)	6.7852(6)	8.4537(13)
<i>c</i> , Å	7.3050(10)	18.6971(17)	19.890(3)
α (°)	95.576(2)	90.00	79.211(2)
β (°)	95.608(2)	102.382(2)	83.767(2)
γ (°)	90.674(2)	90.00	87.403(2)
Volume (Å <sup>3</sup> )	1003.1(2)	2249.1(3)	1239.8(3)
Z	2	4	2
Calculated density (mg·m <sup>-3</sup> )	1.600	1.457	1.712
Absorption coefficient (mm <sup>-1</sup> )	0.632	5.006	0.953
F (000)	500	1024	648
Crystal size (mm)	0.20×0.20×0.18	0.42×0.13×0.08	0.40×0.40×0.28
Index range	-8≤h≤8	-16≤h≤21	-9≤h≤9
	-9≤k≤6	-5≤k≤8	-11≤k≤11
	-27≤1≤26	-21≤l≤22	-19≤l≤26
Reflections collected / unique	7200 / 4959	6812/3860	8450 / 5663
<i>R</i> (int)	0.0212	0.1163	0.0248
Completeness (%)	98.0	98.8	97.5
Data / restraints / parameters	4959 / 0 / 262	3860/0/273	5663 / 0 / 307
Goodness-of-fit on $F^2$	1.138	0.952	1.025
Final <i>R</i> indices [I>2sigma(I)]	$R_1 = 0.0403$	$R_1 = 0.0846$	$R_1 = 0.0580$
	$wR_2 = 0.1348$	$wR_2 = 0.1031$	$wR_2 = 0.1672$
		0.201 and $0.207$	0.025 and 0.590

Table 1. Crystallographic data and refinement details for 1-3.

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

1			
Ca(1)-O(2W)	2.3984(14)	Ca(1)-O(4W)	2.4110(15)
Ca(1)-O(1)	2.4448(13)	Ca(1)-O(1)A	2.4718(13)
Ca(1)-O(3W)	2.4990(14)	Ca(1)-O(1W)	2.5346(13)
Ca(1)-O(2)B	2.5371(13)	Ca(1)-O(1W)B	2.5794(14)
O(2W)-Ca(1)-O(4W)	139.55(5)	O(4W)-Ca(1)-O(3W)	73.36(5)
O(2W)-Ca(1)-O(1)	118.06(5)	O(1)-Ca(1)-O(3W)	149.96(5)
O(4W)-Ca(1)-O(1)	77.22(5)	O(2W)-Ca(1)-O(1W)	77.03(5)
O(2W)-Ca(1)-O(3W)	82.22(5)	O(4W)-Ca(1)-O(1W)	142.48(5)
O(1)-Ca(1)-O(1W)	75.89(4)		
2			
Ca(1)-O(1)	2.366(6)	Ca(1)-O(2)A	2.391(6)
Ca(1)-O(7)	2.412(6)	Ca(1)-O(8)	2.419(6)
Ca(1)-O(4)	2.501(6)	Ca(1)-O(5)	2.529(6)
Ca(1)-O(2)B	2.530(6)	Ca(1)-O(1)B	2.550(6)
O(3)-Ca(1)-O(5)	82.42(8)	O(3W)-Ca(1)-O(1W)	139.83(10)
O(3)-Ca(1)-O(3W)	98.46(10)	O(3)-Ca(1)-O(2W)	83.16(11)
O(5)-Ca(1)-O(3W)	78.84(10)	O(5)-Ca(1)-O(2W)	143.11(10)
O(3W)-Ca(1)-O(2W)	69.97(11)	O(1W)-Ca(1)-O(2W)	70.16(11)
O(3)-Ca(1)-O(1W)	81,42(9)	O(5)-Ca(1)-O(1W)	139.90(10)
3	$\bigvee$		
Ca(1)-O(3)	2.385(2)	Ca(1)-O(5)	2.408(2)
Ca(1)-O(3W)	2.427(3)	Ca(1)-O(6)A	2.429(2)
Ca(1)-O(2)B	2.437(2)	Ca(1)-O(1W)	2.492(3)
Ca(1)-O(2W)	2.550(3)	Ca(1)-O(5)A	2.680(3)
O(3)-Ca(1)-O(5)	82.42(8)	O(1W)-Ca(1)-O(2W)	70.16(11)
O(3)-Ca(1)-O(3W)	98.46(10)	O(3)-Ca(1)-O(2W)	83.16(11)
O(5)-Ca(1)-O(3W)	78.84(10)	O(3)-Ca(1)-O(1W)	81.42(9)
✓ O(5)-Ca(1)-O(2W)	143.11(10)	O(5)-Ca(1)-O(1W)	139.90(10)
O(3W)-Ca(1)-O(2W)	69.97(11)	O(3W)-Ca(1)-O(1W)	139.83(10)

Symmetry transformations used to generate equivalent atoms for **1**: A -x+2, -y+1, -z, B -x+1, -y+1, -z; for **2**: A x, y+1, z, B -x+1, y+1/2, -z+3/2, C -x+1, y-1/2, -z+3/2, D x, y-1, z; for **3**: A -x+1, -y+2, -z+1, B -x+2, -y+2, -z+1

Table 3. Bond lengths	(Å) and angles	(°) of hydrogen	-bond for 1-3

D-Huua	d(D-H)	d(HIIII)	d(DIIIA)	∠DHA
1				
O1W-H1WA…O5	0.97	2.01	2.980(2)	174
O1W-H1WB…O5	0.97	2.03	2.784(2)	133
O2W-H2WA····O4	0.96	1.85	2.720(2)	150
O2W-H2WA····O5	0.96	2.40	3.208(2)	142
O3W-H3WB…O6	0.96	2.19	2.985(2)	139
O4W-H4WA····O4	0.96	2.09	2.912(2)	143
O4W-H4WB…O4	0.96	1.94	2.815(2)	150
2			(	20
O8-H8C…O9	0.85	1.907	2.724	-161
O9-H9F…O4	0.85	1.989	2.838(3)	176
O9-H9G…O5	0.85	2.168	3.017(2)	176
3		$\sim$	$\mathbb{N}$	
O1W-H1WB…O6W	0.95	2.29	3.109(8)	144
O2W-H2WA····O6W	0.96	1.95	2.882(10)	163
O2W-H2WB····O3W	0.96	2.52	3.020(5)	113
O3W-H3WA····O5W	0.96	2.12	2.778(5)	125
O5W-H5WA…O6	0.85	2.10	2.697(4)	127
O6W-H6WA…O3	0.85	2.43	2.974(7)	122
O6W-H6WB…Cl3	0.85	2.59	3.270(8)	138
O5W-H5WB-yCl5	0.85	2.54	3.289(4)	148



Figure 1. Coordination environment and polyhedron of Ca(II) and coordination modes in **1**. Hydrogens are omitted for clarity.



Figure 2. Fragment of the 1D chain and 2D layer. Hydrogens are omitted for clarity.



Figure 3. Coordination environment, polyhedron of Ca(II) and coordination modes in **2**. Hydrogens omitted for clarity.

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Figure 4. Fragment of the 1D chain and 2D layer.

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Figure 5. Coordination environment and polyhedron of Ca(II) and coordination modes in **3**. Hydrogens omitted for clarity.



Figure 6. Fragment of the 1D chain and 2D layer.



Figure 7. The bond length between chlorine and nearest oxygen in 1-3.



### **Graphical abstract**

