

## 两个基于三嗪衍生物和主族金属的一维配位聚合物

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**摘要:** 本文作者采用 2-羟基-4,6-二(2-吡啶基)-1,3,5-三嗪在室温下分别与氯化钠和氯化钙反应,得到了 2 种配合物 $[\text{Na}(\text{OBPT})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  (**1**)和 $[\text{Ca}(\text{OBPT})(\text{H}_2\text{O})_2\text{Cl}]\cdot \text{H}_2\text{O}$  (**2**),并通过元素分析、红外、热重分析、粉末衍射和单晶衍射等方法对其结构进行了表征。单晶结构表明化合物 **1** 属于正交晶系的  $Pbca$  空间群,化合物 **2** 属于三斜晶系的  $P\bar{1}$  空间群。2 个化合物都是一维链状结构,配体作为桥连配体采用三齿螯合和单齿配位的模式与 2 个金属配位。其中,化合物 **1** 中相邻 2 个配体的三嗪环几乎垂直,而化合物 **2** 中相邻 2 个配体的三嗪环则基本是共面的。

**关键词:** 配合物; 1,3,5-三嗪; 碱金属; 一维链

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## One Dimensional Coordination Polymers Based on Main Group Metal Ions and 1,3,5-Triazine Derivative

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**Abstract:** Two coordination compounds  $[\text{Na}(\text{OBPT})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Ca}(\text{OBPT})(\text{H}_2\text{O})_2\text{Cl}]\cdot \text{H}_2\text{O}$  (**2**) were obtained at room temperature by reactions of 4,6-bis(2-pyridyl)-1,3,5-triazine-2-ol (HOBPT) with NaCl and  $\text{CaCl}_2$ , respectively. They were characterized by elemental analysis, FTIR, powder X-ray diffraction analyses and single-crystal X-ray diffraction analyses. Single-crystal X-ray diffraction analyses indicate that complex **1** crystallizes in the orthorhombic  $Pbca$  space group, while complex **2** crystallizes in the triclinic  $P\bar{1}$ . In complex **1**, the sodium ion is coordinated with three nitrogen atoms from one ligand, a deprotonated hydroxyl oxygen atom from another ligand and a coordinated water molecule to form a one-dimensional structure. Similarly, compound **2** is also one-dimensional chain structure, however, the calcium ion is seven coordinated with one more coordinated water molecule and one chloride ion. Interestingly, the two triazine rings of the neighbouring ligands of **1** are almost vertical while those of **2** are coplanar. CCDC: 824484, **1**; 824485, **2**.

**Key words:** coordination compound; 1,3,5-triazine; alkali metal; 1D chain

## 0 Introduction

Many complexes based on polypyridyl ligands have been reported<sup>[1]</sup>. Among them, the rigid multi-dentate polypyridyl ligands containing a triazine ring as a bridge have attracted great attention due to their

coordination diversity<sup>[2-3]</sup>. The most familiar one of these kinds of ligands is tri (2-pyridyl)-1,3,5-triazine (TPT), which can act as tridentate, bis-bidentate, tri-bidentate ligand<sup>[2-7]</sup>. Although coordination chemistry of the symmetrical TPT has been well explored, the report on that of the asymmetric ligands containing triazine ring

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is still rare<sup>[8-11]</sup>. During the research, the asymmetrical polypyridyl 1,3,5-triazine derivatives with one pyridyl group being replaced by other functional group such as hydroxyl, amino, phenyl or sulphydryl group have attracted much our attention. Using hydroxyl group to replace one of the pyridyl groups in TPT, we obtained 4,6-bis (2-pyridyl)-1,3,5-triazin-2-ol (HOBPT), and studied its coordination behaviors.

The ligand 4,6-bis (2-pyridyl)-1,3,5-triazin-2-ol (HOBPT) has six potential coordinate sites, it may offer more than one coordination modes, such as tridentate terpyridine-like, bidentate bipyridine-like and tetradentate bis-bipyridine-like modes. Besides, the OH group can deprotonate and further coordinate to metal ions or form hydrogen bonds with the donated groups. When combining with transition metals, the ligand always acts as tridentate or bis-bidentate ligand which is dependent on the metal/ligand ratio and the reaction conditions, in which its hydroxyl group is uncoordinated. We reported before a hydrophobic, cubic, nanosize cation  $[\text{Co}(\text{H}_2\text{O})_6 \subset \text{Co}_8(\text{OBPT})_{12}]^{6+}$  based on this ligand, in which the OBPT ligand adopts a bis-bipyridine-like binding mode with the capability of bridging two cobalt(II) ions in a chelating manner<sup>[12-14]</sup>. To exploit the new motifs of this kind of ligand, we extend the coordination chemistry of this ligand to alkali metals or alkaline earth metals, that has never been reported and hope that the ligand could possibly generate new architectures. Herein, we report two new complexes,  $[\text{Na}(\text{OBPT})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Ca}(\text{OBPT})(\text{H}_2\text{O})_2\text{Cl}] \cdot \text{H}_2\text{O}$  (**2**), in which the ligands act as bridges in the *N,N,N*-tridentate-chelating and *O*-monodentate tetradentate mode to form 1D chain structures.

## 1 Experimental

### 1.1 General methods

The reagents and solvents employed were commercially available and were used as received without further purification. The C, H, and N microanalyses were carried out with a Vario EL elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range of 400~4 000  $\text{cm}^{-1}$  on a

Bruker TENSOR 27 spectrometer.  $^1\text{H}$  NMR spectra were recorded on a Varian 300 MHz spectrometer at 25  $^{\circ}\text{C}$ . Electron spray ionization (ESI) mass spectra were obtained on a LCQ DECA XP quadrupole ion trap mass spectrometer with methanol as the carrier solvent. Powder X-ray diffraction patterns were recorded on a D8 ADVANCE diffractometer with  $\text{Cu } K\alpha_1$  radiation ( $\lambda=0.154\,06\text{ nm}$ ) at a scanning rate of  $4^{\circ} \cdot \text{min}^{-1}$  with  $2\theta$  ranging from  $3^{\circ}$  to  $40^{\circ}$ . Thermogravimetric data were collected on a Netzsch TGS-2 analyzer in nitrogen at a heating rate of  $10^{\circ}\text{C} \cdot \text{min}^{-1}$ .

### 1.2 Preparations

Synthesis of HOBPT: HOBPT was prepared according to previously reported procedures<sup>[15]</sup>, yield 56%. ESI-MS:  $m/z=250$ ; FTIR (KBr,  $\text{cm}^{-1}$ ): 3 755 (w), 3 240 (s), 3 064 (m), 2 924 (m), 1 686 (m), 1 645 (m), 1 582 (vs), 1 545 (vs), 1 487 (vs), 1 431 (vs), 1 379 (s), 1 290 (w), 1 257 (w), 1 142 (w), 1 028 (w), 1 001 (m), 806 (s), 754 (s), 675 (s), 627 (s), 584 (s).  $^1\text{H}$  NMR data ( $\text{DMSO}-d_6$ , ppm): 8.52 (d,  $J=3.91\text{ Hz}$ , 2H), 8.41 (d,  $J=7.87\text{ Hz}$ , 2H), 7.94 (t, 2H), 7.48 (t, 2H).

Synthesis of  $[\text{Na}(\text{OBPT})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  (**1**): To a suspension of HOBPT (0.125 g, 0.5 mmol) in 10 mL of ethanol was added to the solution of NaCl (0.030 g, 0.5 mmol) in 10 mL distilled water. The resulting mixture was stirred for 1 hour and then filtered. The obtained colorless filtrate was allowed to stand at ambient temperature for a period of about 1 week, giving 0.14 g (86% yield) of colorless needlelike single crystals suitable for structural determinations. Anal. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_5\text{NaO}_4(\%)$ : C 47.71, H 4.31, N 21.40; Found(%): C 47.54, H 4.20, N 21.34. FTIR (KBr,  $\text{cm}^{-1}$ ): 3 436 (s), 3 244 (m), 1 647 (w), 1 580 (vs), 1 543 (vs), 1 487 (vs), 1 431 (m), 1 381 (s), 1 290 (w), 1 259 (w), 1 140 (w), 1 097 (w), 1 049 (w), 1 001 (m), 862 (w), 841 (w), 806 (m), 754 (m), 708 (w), 675 (w), 625 (w).

Synthesis of  $[\text{Ca}(\text{OBPT})(\text{H}_2\text{O})_2\text{Cl}] \cdot \text{H}_2\text{O}$  (**2**): A similar procedure was taken with  $\text{CaCl}_2$  (0.055 g, 0.5 mmol) instead of NaCl. Then 0.158 g colorless blocky-shaped single crystals of **2** were obtained with a yield of 83%. Anal. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{CaClN}_5\text{O}_4(\%)$ : C 41.11, H 3.72, N 18.44; Found(%): C 41.04, H 3.84, N 18.35. FTIR (KBr,  $\text{cm}^{-1}$ ): 3 369 (s), 1 674 (w), 1 643 (w), 1 543 (s),

1 477 (s), 1 433 (m), 1 381 (m), 1 296 (w), 1 258 (w), 1 099 (w), 1 053 (w), 1 007 (w), 864 (w), 804 (m), 752 (w), 712 (w), 681 (w), 633 (w).

### 1.3 Crystal structure determination

Diffraction data for the complexes were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.071\ 073$  nm). Absorption corrections were applied using SADABS<sup>[16]</sup>. The structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXS-97 and SHELXL-97

programs, respectively<sup>[17-18]</sup>. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C-H 0.096 nm and N-H 0.086 nm). The hydrogen atoms of the coordinated water molecules were located from difference maps and refined with isotropic temperature factors. Crystal data, as well as details of data collection and refinement for the complexes, are summarized in Table 1. Selected bond distances, bond angles and hydrogen bonds are listed in Table 2 and 3, respectively.

**Table 1** Crystal data and structure parameters for the complexes

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>13</sub> H <sub>14</sub> N <sub>5</sub> NaO <sub>4</sub>	C <sub>13</sub> H <sub>9</sub> CaClN <sub>3</sub> O <sub>4</sub>
Formula weight	327.28	379.82
$T / K$	293(2)	293(2)
$\lambda$ (Mo $K\alpha$ ) / nm	0.071 073	0.071 073
Crystal system	Orthorhombic	Triclinic
Space group	$Pbca$	$P\bar{1}$
$a$ / nm	1.629 4(2)	0.837 4(1)
$b$ / nm	0.953 1(1)	0.867 7(1)
$c$ / nm	1.927 0(3)	1.145 2(1)
$\alpha / (^\circ)$		95.627(2)
$\beta / (^\circ)$		94.101(2)
$\gamma / (^\circ)$		104.880(2)
$V / \text{nm}^3$	2.992 7(7)	0.796 3(1)
$Z$	8	2
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.453	1.584
$\mu / (\text{mm}^{-1})$	0.134	0.591
$F(000)$	1360	392
Crystal size / mm	0.31×0.11×0.09	0.29×0.26×0.18
Method of collecting reflections	$\varphi$ - $\omega$	$\varphi$ - $\omega$
$\theta$ range for data collection / $(^\circ)$	2.46~25.99	1.80~26.00
Completeness to $\theta=26.00^\circ$ / %	99.70	99.60
Reflns. collected / unique ( $R_{int}$ )	9 607 / 2 928 (0.039 5)	4 235 / 3 121 (0.012 4)
Observed reflns ( $I \geq 2\sigma(I)$ )	2 091	2 626
Parameters refined	210	221
Goodness-of-fit on $F^2$	1.006	1.003
Final $R$ indices ( $I \geq 2\sigma(I)$ )	$R_1=0.052\ 2$ , $wR_2=0.126\ 6$	$R_1=0.040\ 1$ , $wR_2=0.129\ 7$
Maximum peak / ( $\text{e} \cdot \text{nm}^{-3}$ )	256	694
Minimum peak / ( $\text{e} \cdot \text{nm}^{-3}$ )	-180	-543

**Table 2** Selected bond lengths (nm) and angles ( $^\circ$ ) for compound **1** and **2**

<b>1</b>					
Na1-O1 <sup>i</sup>	0.230 0(2)	Na1-O1W	0.237 4(2)	Na1-N2	0.239 7(2)
Na1-N5	0.249 6(2)	Na1-N1	0.253 3(2)		

Continued Table 1

O1i-Na1-O1W	85.33(6)	O1i-Na1-N2	146.55(7)	O1W-Na1-N2	125.35(7)
O1i-Na1-N5	93.83(7)	O1W-Na1-N5	108.57(7)	N2-Na1-N5	65.85(6)
O1i-Na1-N1	126.30(7)	O1W-Na1-N1	100.15(6)	N1-Na1-N2	66.54(6)
N1-Na1-N5	132.35(7)				
<b>2</b>					
Ca1-N1	0.257 5(2)	Ca1-N2	0.254 3(2)	Ca1-N5	0.262 3(2)
Ca1-O1W	0.236 5(2)	Ca1-O2W	0.233 1(2)	Ca1-Cl1	0.271 3(1)
Ca1-O1 <sup>ii</sup>	0.248 5(1)				
N2-Ca1-N1	62.87(5)	N1-Ca1-N5	125.02(6)	N2-Ca1-N5	62.95(6)
O1W-Ca1-N5	77.65(6)	O2W-Ca1-N5	87.76(7)	N2-Ca1-Cl1	87.16(4)
N1-Ca1-Cl1	89.66(4)	N5-Ca1-Cl1	96.36(6)	O1W-Ca1-Cl1	95.86(6)
O2W-Ca1-Cl1	171.87(4)	O1W-Ca1-N1	156.00(6)	O1W-Ca1-N2	140.56(6)
O2W-Ca1-N2	88.49(5)	O2W-Ca1-N1	82.24(5)	O2W-Ca1-O1W	91.87(8)
O1 <sup>ii</sup> -Ca1-N1	82.28(5)	O1 <sup>ii</sup> -Ca1-N2	144.92(5)	O1 <sup>ii</sup> -Ca1-N5	152.06(6)
O1 <sup>ii</sup> -Ca1-Cl1	88.94(4)	O1W-Ca1-O1 <sup>ii</sup>	74.52(6)	O2W-Ca1-O1 <sup>ii</sup>	90.68(5)

Symmetry cod:1: <sup>i</sup>  $x+1/2, y, -z+3/2$ ; 2: <sup>ii</sup>  $x, y+1, z$ .

Table 3 Hydrogen bonding for compounds 1 and 2

Doner-H...Acceptor	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
<b>Compound 1</b>				
O1W-H1WA...N4 <sup>i</sup>	0.090	0.199	0.286 1(2)	163.4
O1W-H1WB...N3 <sup>iii</sup>	0.090	0.203	0.287 2(3)	154.8
O2W-H2WA...O2W <sup>iv</sup>	0.090	0.203	0.290 5(6)	162.8
O2W-H2WB...O1 <sup>v</sup>	0.090	0.221	0.304 4(3)	153.2
O2W'-H2WC...O3W'	0.090	0.199	0.282 2(4)	153.6
O3W-H3WA...O3W <sup>vi</sup>	0.090	0.217	0.287 4(5)	134.3
O3W'-H3WD...O1W	0.091	0.196	0.284 3(3)	165.4
<b>Compound 2</b>				
O1W-H1WA...N4 <sup>ii</sup>	0.084	0.194	0.275 9(2)	167.0
O1W-H1WB...Cl1 <sup>vii</sup>	0.084	0.239	0.322 2(2)	169.5
O2W-H2WA...O3W <sup>viii</sup>	0.083	0.189	0.269 3(2)	162.9
O2W-H2WB...N3 <sup>ix</sup>	0.089	0.200	0.288 5(2)	176.6
O3W-H3WA...O1 <sup>ii</sup>	0.084	0.229	0.296 8(2)	138.2
O3W-H3WB...Cl1	0.083	0.234	0.315 9(2)	171.0

Symmetry codes: 1: <sup>i</sup>  $x+1/2, y, -z+3/2$ ; <sup>iii</sup>  $-x+1/2, y+1/2, z$ ; <sup>iv</sup>  $-x+1, -y+1, -z+1$ ; <sup>v</sup>  $x+1/2, -y+1/2, -z+1$ ; <sup>vi</sup>  $-x+1, -y, -z+1$ ;2: <sup>ii</sup>  $x, y+1, z$ ; <sup>vii</sup>  $-x+1, -y+2, -z+1$ ; <sup>viii</sup>  $x+1, y, z$ ; <sup>ix</sup>  $-x+1, -y+1, -z$ .

CCDC: 824484, 1; 824485, 2.

## 2 Results and discussion

### 2.1 Crystal structure of 1

Complex **1** crystallizes in an orthorhombic space group Pbca. The single-crystal structure reveals that complex **1** is a one-dimensional chain structure, in which the asymmetric unit contains one sodium ion, one

deprotonated OBPT<sup>-</sup> ligand, one coordinated water molecule and two lattice water molecules. As illustrated in Fig.1, each sodium ion is five coordinated with three nitrogen atoms (two pyridyl nitrogen atom N1 and N5, triazine nitrogen atom N2) from one OBPT ligand, a hydroxyl oxygen atom O1<sup>i</sup> from another ligand (symmetry code: <sup>i</sup> O1:  $x+1/2, y, -z+3/2$ ), and one water molecule. Each OBPT ligand coordinates to two sodium

ions as a bridge, adopting a *N,N,N*-tridentate chelating and *O*-monodentate tetradentate mode, which is different from the complexes of OBPT with transition metals we obtained before. Moreover, the sodium ion also connects with two ligands and therefore complex **1** shows 1D chain structure with the M:L ratio of 1:1. The Na-N distances are 0.253 3(2), 0.239 7(2) and 0.249 6(2) nm, and the Na-O are 0.230 0(2), 0.237 4(2) nm. These bond lengths are comparable to those of sodium complexes<sup>[19-20]</sup>. The triazine rings of adjacent ligands in the chain are almost vertical, with the

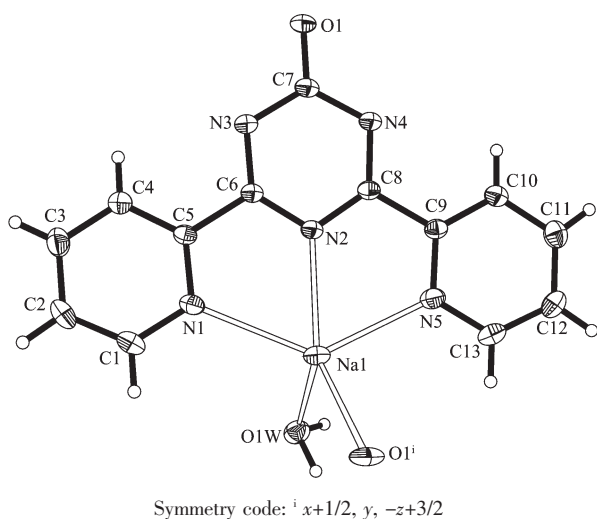


Fig.1 Coordination environment of sodium ion in **1**

dihedral angle of 89.2°.

Furthermore, the coordinated water molecule O1W donates an intramolecular hydrogen bond to the N4<sup>i</sup> (symmetry code: <sup>i</sup>  $x+1/2, y, -z+3/2$ ; O1W...N4 0.286 1 (2) nm) from the triazine ring of neighbouring ligand and further hydrogen bond to the triazine N3<sup>ii</sup> from the adjacent chain (symmetry code: <sup>ii</sup>  $-x+1/2, y+1/2, z$ ; O1W...N3 0.287 3 (3) nm), resulting in a 2D hydrogen-bonding structure on *ab* plane with strong  $\pi$ - $\pi$  interactions between the triazine ring and pyridine ring from neighbouring framework, with a distance of 0.337 6 nm (Fig.2).

There are interesting water chains positioned between the hydrogen-bonding layers mentioned above. Two lattice water molecules O2W and O3W link each other by hydrogen-bonding (O2W...O2W 0.290 5(6) nm, O2W...O3W 0.282 2(4) nm, O3W...O3W 0.287 4 (5) nm) to form a 1D water chain along *b*

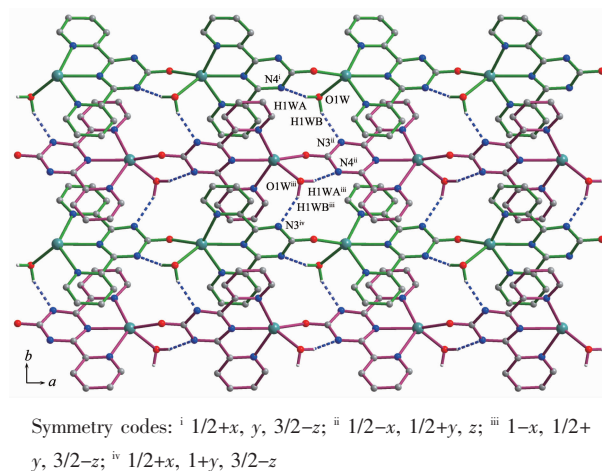


Fig.2 2D framework linked by hydrogen bonds of coordinated water molecule

axis. The positions of hydrogen atoms in lattice water molecules are somewhat disordered, we determined two sets of hydrogen atoms from the diffraction map. The water chains further connect to coordinated O1W molecules and O1 atoms (O3W...O1W 0.284 3(3) nm, O2W...O1 0.304 4 (3) nm) from 2D hydrogen-bonded layers to generate 3D structure.

## 2.2 Crystal structure of **2**

With CaCl<sub>2</sub> instead of NaCl in **1**, we obtained complex **2**. Complex **2** crystallizes in a triclinic  $P\bar{1}$  space group. As shown in Fig.3, each calcium ion is coordinated by three nitrogen atoms from one OBPT ligand, one hydroxyl oxygen atom from another ligand

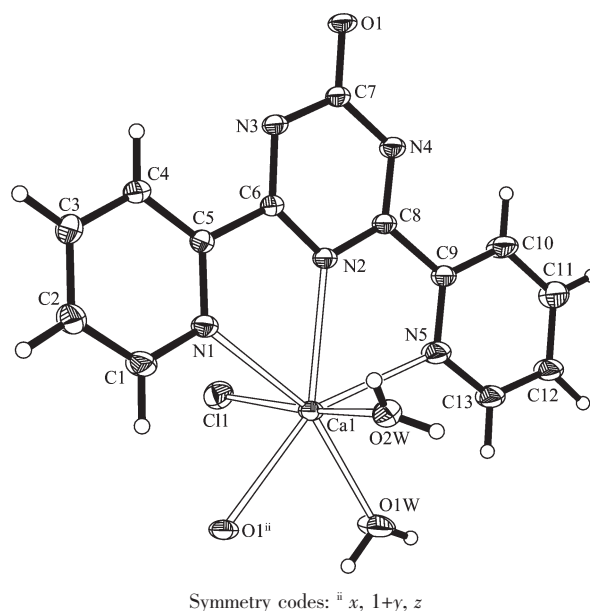
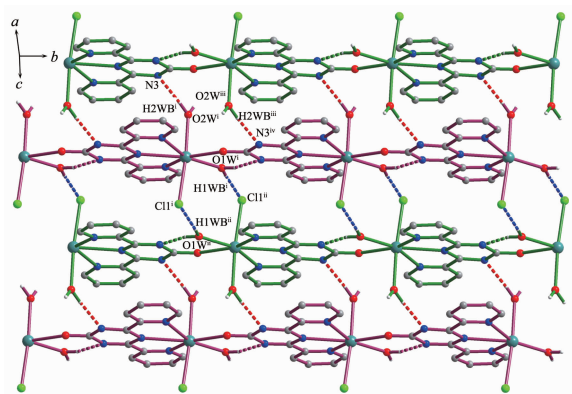


Fig.3 Coordination environment of calcium ion in **2**

(Symmetry code:  $x, 1+y, z$ ), one chloride ion and two coordinated water molecules to furnish a distorted pentagonal bipyramid geometry, in which O2W and Cl1 posit on the axis with O2W-Ca1-Cl1 171.85(4)°. Complex **2** also shows 1D chain structure with O1W donates hydrogen bond to triazine N4<sup>iii</sup> (symmetry code: <sup>iii</sup>  $x, y+1, z$ ; O1W...N4 0.276 0(2) nm) to form intramolecular hydrogen bonds, which is similar to complex **1**. The Ca-N distances are 0.257 5(2), 0.254 3(2) and 0.262 3(2) nm, the Ca-O are 0.248 5(1), 0.236 5(2) and 0.233 1(2) nm, the Ca-Cl distance is 0.2712 7(7) nm. These bond lengths are comparable to those of calcium complexes<sup>[21-23]</sup>. Interestingly, the triazine rings of adjacent ligands in the chain are almost coplanar, with the dihedral angle of 0.0°. It is very different from complex **1**, whose dihedral angles of adjacent triazine rings are 89.2°.

In the 1D chain, the OBPT ligands, metal ions and coordinated O1W are almost in the same plane, however, the coordinated O2W and Cl1 are vertically positioned up and down the plane. These chains further link each other via hydrogen bondings (O2W...N3 0.288 5(2) nm, O1W...Cl1 0.322 2(2) nm) into a 2D hydrogen-bonded network on bc plane (Fig.4).



Symmetry codes: <sup>i</sup>  $1-x, 1-y, -z$ ; <sup>ii</sup>  $x, -1+y, -1+z$ ; <sup>iii</sup>  $x, 1+y, z$ ; <sup>iv</sup>  $1-x, 2-y, -z$

Fig.4 2D hydrogen-bonding layer on bc plane

The above 2D layers are then linked by lattice water molecules O3W (O2W...O3W 0.269 3(2) nm, O3W...O1 0.296 8(2) nm, O3W...Cl1 0.315 9(2) nm) to form 3D hydrogen-bonding networks.

### 2.3 Powder X-ray diffraction patterns

From Fig.5 we can find that, the powder XRD

patterns for as synthesized **1** and **2** are well matched with the simulated ones based on the single-crystal analyses, which indicates that the samples are in pure phases.

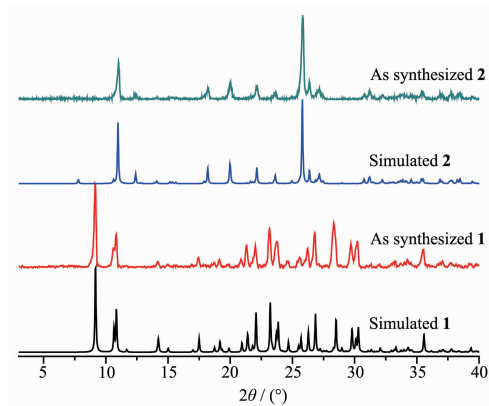


Fig.5 Powder XRD patterns of the simulation based on the single-crystal analyses and as-synthesized complexes

### 2.4 Thermal analyses

Furthermore, thermal gravimetric analyses (TGA) were performed from 20 to 800 °C to examine the lattice water molecules and stability. For **1**, the weight loss of 10.92% in the range of 25~76 °C (Fig.6) corresponds to the loss of two lattice water molecules (calcd. 11.00%), indicating that the guest water molecules were completely removed at 76 °C. Increasing temperature up to 369 °C, the weight loss of 16.49% corresponds to the loss of three water molecules (calcd. 16.5%, two lattice and one coordinate water molecule). For **2**, three step processes are observed. Firstly, from 25 to 60 °C, the weight is not changed. Secondly, from 60~100 °C, weight loss of 10.36% corresponds to the loss of two water molecules (calcd. 10.48%). Thirdly, the weight

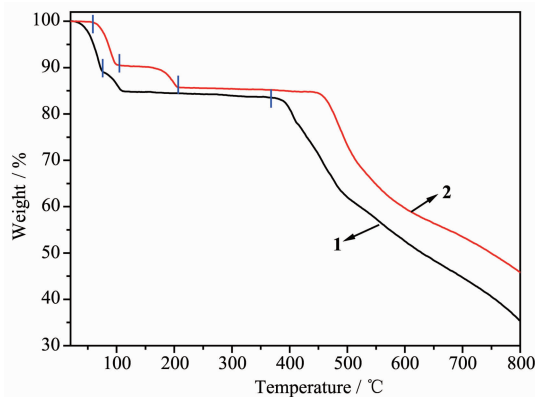


Fig.6 TGA curves for the complex **1** and **2**



loss of 14.2% up to 205 °C corresponds to the loss of all the three water molecules (one lattice and two coordinate water molecule, calcd. 14.22%). From Fig.6 we can find out that both of the two complexes are stable up to 350~450 °C.

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