

## 2,2'-二硫代二苯甲酸、2,2'-二羧苯基硫醚及含氮配体 构筑的 2 个配合物的合成、结构与热稳定性研究

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**摘要:** 使用 2,2'-二硫代二苯甲酸和 2,2'-联吡啶(2,2'-bipy)、硝酸铜在水热条件下发生的原位反应合成了一个铜配合物, 即[Cu<sub>2</sub>(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>] (**1**)(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S=2,2'-二羧苯基硫醚, C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>=2,2'-联吡啶); 然后又利用 2,2'-二硫代二苯甲酸和非咯啉(phen)、氯化钙在水溶液中合成了一个钙配合物, 即[[Ca(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S)<sub>2</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (**2**)(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S=2,2'-二硫代二苯甲酸根, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>=非咯啉), 并对它们分别进行了元素分析、红外光谱、热稳定性、X 射线粉末衍射和 X 射线单晶衍射的表征。结果表明: 配合物 **1** 由 2,2'-二羧苯基硫醚配体连接形成了一个双核的化合物, 通过氢键和氮杂环之间的  $\pi \cdots \pi$  作用形成三维超分子网络结构。配合物 **2** 由二硫代二苯甲酸配体桥联形成了一个一维链状结构, 通过氢键和氮杂环之间的  $\pi \cdots \pi$  作用也形成三维超分子网络结构。并且, 对这 2 个配合物的热稳定性分别进行了研究。

**关键词:** 配合物; 2,2'-二硫代二苯甲酸; 2,2'-二羧苯基硫醚; 晶体结构;  $\pi \cdots \pi$  作用

中图分类号: O614.121; O614.23+1 文献标识码: A 文章编号: 1001-4861(2014)11-2684-07

DOI: 10.11862/CJIC.2014.536

## Synthesis, Crystal Structure and Thermal Properties of Two Complexes Constructed by 2,2'-Dithiosalicylic Acid, Bis(2-carboxyphenyl)sulfide and N-Donor Ligands

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**Abstract:** Hydrothermal reaction *in-situ* of 2,2'-dithiosalicylic acid, 2,2'-bipy and copper dinitrate offers a Cu(II) complex, [Cu<sub>2</sub>(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>] (**1**) (C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S=bis(2-carboxyphenyl) sulfide, C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>=2,2'-bipy); while [[Ca(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S)<sub>2</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (**2**) (C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>S=2,2'-dithiosalicylate C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>=phen) was synthesized by mixing 2, 2'-dithiosalicylic acid, phen and calcium chloride; after that they were characterized by elemental analysis, IR, TGA, PXRD and X-ray single crystal diffraction. Complex **1** has a dinuclear structure and finally forms a three-dimensional supramolecular structure by hydrogen bond and  $\pi \cdots \pi$  stacking interactions between 2,2'-bipy molecules. Complex **2** has a one-dimensional chain structure, which are linked by 2,2'-dithiosalicylate ligands, and further extends into a three-dimensional supramolecular structure by hydrogen bond and  $\pi \cdots \pi$  stacking interactions between phen molecules. Furthermore, the thermal stabilities properties of the complexes are investigated in detail. CCDC: 1000615, **1**; 1000614, **2**.

**Key words:** complex; 2,2'-dithiosalicylic acid; bis(2-carboxyphenyl) sulfide; crystal structure;  $\pi \cdots \pi$  stacking interactions

收稿日期: 2014-07-26。收修改稿日期: 2014-08-26。

国家自然科学基金(No.21271055)和广东省基金(No.2011B090400415)资助项目。

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## 0 Instruction

Crystal engineering of metal-organic supramolecular architecture, which employs covalent linkage and non-covalent (supramolecular) interactions such as hydrogen bonding or  $\pi\cdots\pi$  stacking interactions as well as van der Waals forces, has received growing attention over the past few years<sup>[1-5]</sup>. The considerable interest is driven to a large extent owing to their rich topological structures and potential applications in the electrical conductivity, chemical absorption, ion-exchange, catalysis, biology, nonlinear optics, molecular magnets and others<sup>[6-10]</sup>. However, up to now, the control of product architecture still remains a major challenge in this field due to the fact that the structure, functionality and stabilization of the overall supramolecular complexes is frequently influenced by the type and spatial disposition of the ligand binding site, the metal-to-ligand ratio, the stereoelectronic preferences of the metal ion as well as reaction pathways. In relation to the ligands, excellent organic building blocks, most typically including carboxylic acids and their derivatives, and neutral N-donor molecules and their derivatives, have been widely used for the assembly of new crystalline solids<sup>[11-13]</sup>.

The multifunctional thiocarboxylic acid and its derivatives, which have various coordination modes, may link metal centers through both carboxylate groups and the S atom into different extended architectures<sup>[14]</sup>. The carboxylate group can coordinate in multiple ways, either as a chelating ligand or as a bridging ligand with different coordination numbers to various metal cations, resulting in the assembly of different supramolecular complexes. In our previous work, we have reported an Ag(I) coordination polymer with sulfanediyldiacetic acid ligand, in which the two carboxylate O atoms at each end of the sulfanediyldiacetate ligand are distinguished by two coordination modes, one mode being monodentate and the other bridging two Ag(I) cations. It also obviously observed that both carboxylate groups and the S atoms are involved in the coordination<sup>[15]</sup>. In addition, most of the N-donor molecules and their derivatives have

been widely used as the secondary ligands because of their rigid skeletons and the structures formed are more predictable<sup>[13]</sup>. Now, based on the use of thiodicarboxylate as a ligand, we have chosen 2,2'-dithio-salicylic acid to prepare the new supramolecular complexes. Disulfide bridging phenyl carboxylate ligands possess flexibility owing to the presence of -S-S- linkages between the phenyl rings and can adopt various conformations according to geometric requirements when they react with different metal salts, the flexible and multifunctional coordination sites provide a high likelihood for build novel coordination frameworks. On the other hand, disulfides are desirable objects for the in situ metal/ligand reactions because of versatile S-S transformations through the facile cleavage of S-S<sup>[16]</sup>. In this context, we present the syntheses, crystal structures and the properties of the two complexes, namely  $[\text{Cu}_2(\text{C}_{14}\text{H}_8\text{O}_4\text{S})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$  (**1**) and  $\{[\text{Ca}(\text{C}_{14}\text{H}_8\text{O}_4\text{S}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot (\text{H}_2\text{O})_2\}_n$  (**2**), which incorporates 2,2'-bipy and phen ligands respectively.

## 1 Experimental

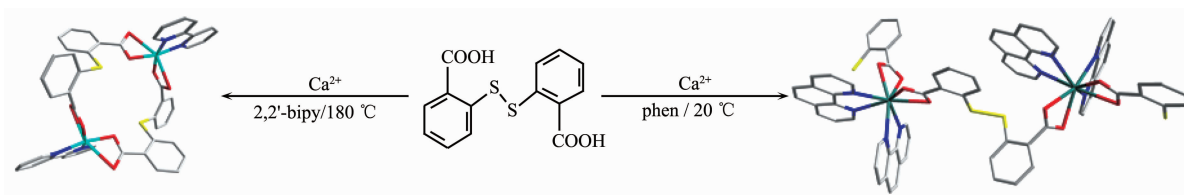
### 1.1 Reagent and instruments

All the reagents were analytical reagent grade and used without further purification. Elemental analyses were performed on a CARLO ERBA 1106 analyzer. The FT-IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer using KBr pellet at a resolution of  $0.5\text{ cm}^{-1}$  ( $400\sim 4\,000\text{ cm}^{-1}$ ). TGA analysis were measured on a PERKIN ELMER TG/DTA 6300 thermogravimetric analyzer under either static air condition or flowing  $\text{N}_2$  atmosphere with a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  starting at ambient temperature and heating up to  $800\text{ }^\circ\text{C}$ , using sample weight of  $1\sim 5\text{ mg}$ . Powder X-ray diffraction (PXRD) patterns were measured at  $293\text{ K}$  on a Bruker D8 diffractometer ( $\text{Cu K}\alpha$ ,  $\lambda=0.154\,059\text{ nm}$ ). The suitable single crystal of these complexes was employed for data collection on a Bruker P4 diffractometer with graphite monochromatized  $\text{Mo K}\alpha$  ( $\lambda=0.071\,073\text{ nm}$ ).

### 1.2 Syntheses of the complexes

#### 1.2.1 Synthesis of $[\text{Cu}_2(\text{C}_{14}\text{H}_8\text{O}_4\text{S})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ (**1**)

The complex was prepared by the addition of

Scheme 1 Preparation of complexes **1** and **2**

2,2'-bipy (20 mmol) and copper dinitrate trihydrate (20 mmol) to a hot aqueous solution (10 mL) of 2,2'-dithiosalicylic acid (20 mmol). The mixture was sealed in a 50 mL Teflon-lined stainless steel bomb and held at 423 K for 72 h. The bomb was cooled naturally to room temperature, and blue crystals were obtained from the filtered solution after several days (Scheme 1). Analysis calculated for  $C_{48}H_{32}N_4O_8S_2Cu_2$ (%): C 58.59, H 3.28, N 5.69; Found (%): C 58.58, H 3.30, N 5.70. IR (KBr,  $cm^{-1}$ ): 3 463(s), 3 411(s), 3 063(w), 1 602(s), 1 498(w), 1 469(w), 1 437(m), 1 376(s), 1 151(m), 1 029(m), 844(m), 751(m), 650(m).

### 1.2.2 Synthesis of $\{[Ca(C_{14}H_8O_4S_2)(C_{12}H_8N_2)] \cdot (H_2O)_2\}_n$ (**2**)

A ethanol/water solution (10 mL) of calcium chloride dihydrate (20 mmol) and phen (20 mmol) were slowly added to an aqueous solution (20 mL) of 2,2'-dithiosalicylic acid (20 mmol), and the pH value was adjusted to 7 with  $0.1 \text{ mol} \cdot L^{-1}$  sodium hydroxide solution. The resulting solution was stirred for 40 min at room temperature, and then filtered. Colorless single crystals were obtained from the filtrate at room temperature over five days (Scheme 1). Analysis calculated for  $C_{38}H_{28}N_4O_6S_2Ca$ (%): C 61.60, H 3.80, N 7.56; Found (%): C 61.61, H 3.81, N 7.55. IR (KBr,

$cm^{-1}$ ): 3 523(s), 3 441(s), 3 057(w), 1 613(s), 1 519(w), 1 427(w), 1 332(s), 1 217(m), 1 076(m), 856(m), 727(m).

### 1.3 X-ray crystallographic determination

The suitable single crystal of these complexes was employed for data collection on a Bruker P4 diffractometer with graphite monochromatized Mo  $K\alpha$  ( $\lambda=0.071\ 073 \text{ nm}$ ) radiation. All structures were solved by direct method and difference Fourier syntheses. All nonhydrogen atoms were refined by full-matrix least-squares techniques on  $F^2$  with anisotropic thermal parameters. In complex **2**, one of the water molecules is disordered. The water molecule was found to be disordered over two sites, the positions of which were refined with fixed site-occupation factors of 0.5 and 0.5. The H atoms on carbon were placed in calculated positions with C-H  $0.093 \text{ nm}$  or  $0.097 \text{ nm}$  and  $U(H)=1.2U_{eq}(C)$  in the riding model approximation, and the H atoms of all the other water molecules were located in different Fourier synthesis maps and refined in the riding model approximation. All calculations were carried out with SHELXL 97 program<sup>[17]</sup>. The summary of the crystallographic data for the complexes are provided in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 1000615, **1**; 1000614, **2**.

Table 1 Crystal data and structure parameters for the complexes

Complex	<b>1</b>	<b>2</b>
Formula	$C_{48}H_{32}N_4O_8S_2Cu_2$	$C_{38}H_{28}N_4O_6S_2Ca$
Formula weight	984.02	740.86
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
$a / \text{nm}$	0.871 2(3)	1.323 85(13)
$b / \text{nm}$	1.108 1(4)	1.805 24(18)
$c / \text{nm}$	1.185 6(4)	1.493 41(15)
$\alpha / (^\circ)$	82.213(4)	90
$\beta / (^\circ)$	73.104(4)	105.822 0(10)
$\gamma / (^\circ)$	82.806(4)	90

Continued Table 1

$V / \text{nm}^3$	1.080 6(7)	3.433 8(6)
$Z$	1	4
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.512	1.429
$\mu / \text{mm}^{-1}$	1.141	0.359
$F(000)$	502	15 28
Crystal dimension / mm	0.14×0.13×0.11	0.32×0.25×0.18
$\theta_{\min}, \theta_{\max} / (^\circ)$	2.45, 25.00	1.81, 25.00
Reflections collected	7 128	19 215
Unique reflections ( $R_{\text{int}}$ )	3 806 (0.016 9)	6 051 (0.030 1)
$R, wR$ ( $I > 2\sigma(I)$ )	0.039 7, 0.092 8	0.047 1, 0.126 0
$R, wR$ (all data)	0.047 4, 0.098 0	0.067 4, 0.136 1
Goodness-of-fit (on $F^2$ )	1.031	1.077
$(\Delta\rho)_{\max}, (\Delta\rho)_{\min} / (\text{e} \cdot \text{nm}^{-3})$	769, -1 488	723, -387

Table 2 Selected bond lengths (nm) and angles ( $^\circ$ ) for the complexes

1					
Cu(1)···O(1)	0.260 1(3)	Cu(1)···O(2)	0.194 8(2)	Cu(1)···O(3) <sup>i</sup>	0.196 7(2)
Cu(1)···O(4) <sup>i</sup>	0.254 2(2)	Cu(1)···N(1)	0.200 3(3)	Cu(1)···N(2)	0.199 7(3)
O(1)-Cu(1)-N(1)	113.49(9)	O(1)-Cu(1)-N(2)	98.33(10)	O(1)-Cu(1)-O(2)	55.49(9)
O(1)-Cu(1)-O(3) <sup>i</sup>	98.11(9)	O(1)-Cu(1)-O(4) <sup>i</sup>	148.23(9)	O(2)-Cu(1)-N(1)	167.31(10)
O(2)-Cu(1)-N(2)	93.95(10)	O(2)-Cu(1)-O(3) <sup>i</sup>	93.60(9)	O(2)-Cu(1)-O(4) <sup>i</sup>	103.19(8)
O(3) <sup>i</sup> -Cu(1)-N(2)	163.44(10)	O(3) <sup>i</sup> -Cu(1)-N(1)	94.40(10)	O(3) <sup>i</sup> -Cu(1)-O(4) <sup>i</sup>	56.69(7)
O(4) <sup>i</sup> -Cu(1)-N(1)	89.44(8)	O(4) <sup>i</sup> -Cu(1)-N(2)	107.15(8)	N(2)-Cu(1)-N(1)	80.95(11)
2					
Ca(1)···O(1)	0.237 3(2)	Ca(1)···O(2)	0.265 5(2)	Ca(1)···O(3) <sup>i</sup>	0.248 3(2)
Ca(1)···O(4) <sup>i</sup>	0.245 2(2)	Ca(1)···N(1)	0.253 7(2)	Ca(1)···N(2)	0.262 4(2)
Ca(1)···N(3)	0.253 8(2)	Ca(1)···N(4)	0.252 7(2)		
O(1)-Ca(1)-O(3) <sup>i</sup>	110.86(12)	O(1)-Ca(1)-O(4) <sup>i</sup>	92.14(10)	O(1)-Ca(1)-O(2)	50.89(7)
O(1)-Ca(1)-N(1)	79.06(8)	O(1)-Ca(1)-N(2)	142.97(8)	O(1)-Ca(1)-N(3)	130.95(8)
O(1)-Ca(1)-N(4)	88.42(9)	O(3) <sup>i</sup> -Ca(1)-O(2)	86.95(10)	O(3) <sup>i</sup> -Ca(1)-N(4)	145.97(9)
O(3) <sup>i</sup> -Ca(1)-N(3)	81.30(9)	O(3) <sup>i</sup> -Ca(1)-N(2)	95.22(10)	O(3) <sup>i</sup> -Ca(1)-N(1)	124.81(8)
O(4) <sup>i</sup> -Ca(1)-O(2)	111.63(10)	O(4) <sup>i</sup> -Ca(1)-O(3) <sup>i</sup>	51.22(8)	O(4) <sup>i</sup> -Ca(1)-N(1)	75.03(8)
O(4) <sup>i</sup> -Ca(1)-N(2)	83.99(10)	O(4) <sup>i</sup> -Ca(1)-N(3)	126.78(8)	O(4) <sup>i</sup> -Ca(1)-N(4)	159.80(9)
N(1)-Ca(1)-N(2)	64.33(7)	N(1)-Ca(1)-N(3)	133.85(8)	N(1)-Ca(1)-O(2)	128.96(7)
N(2)-Ca(1)-O(2)	160.86(8)	N(3)-Ca(1)-O(2)	84.37(7)	N(3)-Ca(1)-N(2)	77.19(8)
N(4)-Ca(1)-O(2)	84.18(7)	N(4)-Ca(1)-N(1)	85.27(8)	N(4)-Ca(1)-N(2)	83.46(7)
N(4)-Ca(1)-N(3)	65.19(8)				

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

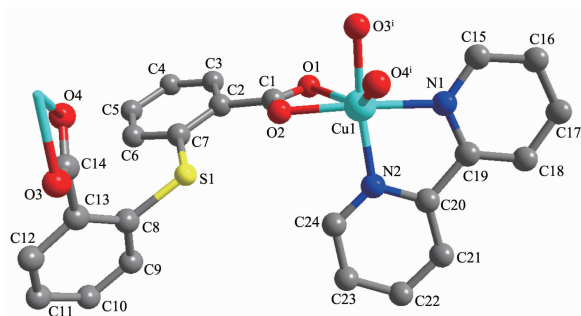
## 2 Results and discussion

### 2.1 Crystal structure of $[\text{Cu}_2(\text{C}_{14}\text{H}_8\text{O}_4\text{S})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ (1)

The *in situ* reaction between 2,2'-dithiosalicylic

acid, 2,2'-bipy and copper dinitrate offers the title Cu(II) complex,  $[\text{Cu}_2(\text{C}_{14}\text{H}_8\text{O}_4\text{S})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$  (1), in which bis (2-carboxyphenyl) sulfide is generated. The molecular structure of the complex 1 is shown in Fig.1. The X-ray diffraction analysis shows that this complex

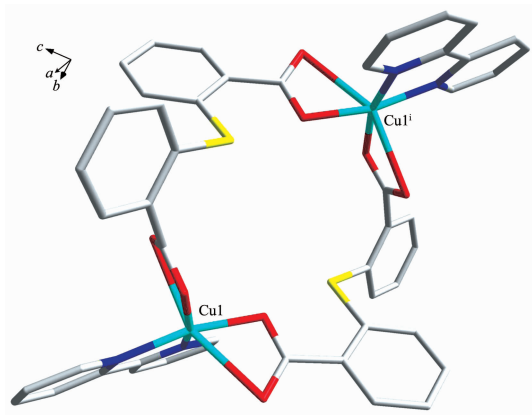
has a dinuclear structure. Each Cu (II) atom is coordinated by four O atoms from two different carboxyphenyl group and two N atoms from one 2,2'-bipy co-ligand, and the local coordination sphere around the Cu(II) ion can be described as a distorted octahedron with a  $\text{CuO}_4\text{N}_2$  chromophore. Atoms O1, O3<sup>i</sup>, O4<sup>i</sup> and N2 comprise the equatorial plane, and atoms O2 and N1 occupy the axial positions ( $\angle \text{O}(2)\text{-Cu}(1)\text{-N}(1)=167.31(10)^\circ$ ; symmetry code is shown in Fig.1). The Cu-N distances fall in the range 0.199 7(3)~0.200 3(3) nm and the Cu-O bond lengths vary from 0.194 8(2) nm to 0.260 1(3) nm (see Table 2).



Symmetry code: <sup>i</sup>  $-x+1, -y+1, -z+1$

Fig.1 Molecular structure of **1**

Adjacent Cu(II) atoms are bridged by the bis(2-carboxyphenyl) sulfide ligand in the bis-bidentate mode, resulting in a dinuclear unit, with the  $\text{Cu}\cdots\text{Cu}$  separation distance of 7.718 nm (Fig.2). Adjacent binuclear units are connected by intermolecular hydrogen bonds, giving rise to a one-dimensional chain structure along a axial direction ( $\text{C23-H23}\cdots\text{O4}^{\text{ii}}$  0.313 2 (4) nm, and  $\text{C21-H21}\cdots\text{O3}^{\text{iv}}$  0.341 4(4) nm; Symmetry codes: <sup>ii</sup>  $x+1, y, z$ ; <sup>iv</sup>  $-x+2, -y+1, -z+1$ ).



Symmetry code: <sup>i</sup>  $-x+1, -y+1, -z+1$

Fig.2 Dinuclear structure of complex **1**

Interestingly, there exist  $\pi\cdots\pi$  stacking interactions between 2,2'-bipy molecules of the adjacent H-bond chains, with approximate centroid distance of 3.711 nm, extending into a two-dimensional supramolecular layer in bc plane. Furthermore, these supramolecular layers are stabilized by interlayer hydrogen bonds, leading to the formation of a three-dimensional supramolecular network (Fig.3).

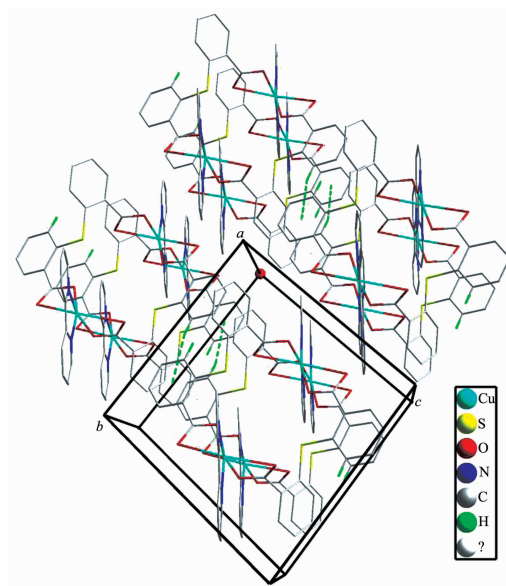
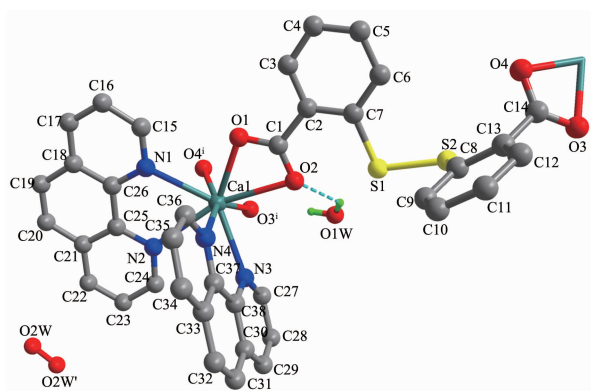


Fig.3 Packing diagram of complex **1**

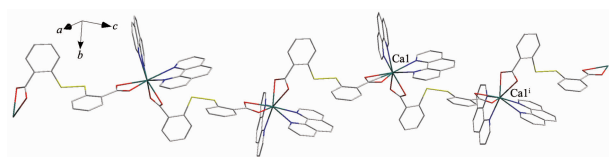
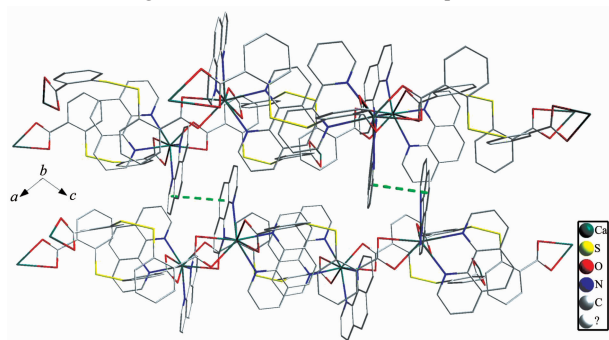
## 2.2 Crystal structure of $[\text{Ca}(\text{C}_{14}\text{H}_8\text{O}_4\text{S}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot (\text{H}_2\text{O})_2$ (**2**)

As depicted in Fig.4, the asymmetric unit of **2** contains a Ca (II) cation, one 2,2'-dithiosalicylate ligand, two phen ligands and two solvate water molecule, one of which is disordered over two sites. The local eight-coordinate environment of the Ca(II) atom is defined by four N-atom donors of two different bidentate phen ligands, four O-atom donors of two bidentate 2,2'-dithiosalicylate ligands. The coordination geometry of the Ca (II) centre can be described as a distorted bicapped triangular prism with two-capped base by the  $\text{Ca1-O2}$  and  $\text{Ca1-N1}$  bonds of 0.265 5(2) and 0.253 7(2) nm, respectively. Atoms O1, O3<sup>i</sup>, O4<sup>i</sup>, and N2, N3, N4 define two equatorial planes, respectively (Symmetry code is shown in Fig.5). The Ca-O distances fall in the range of 0.237 3(2)~0.265 5(2) nm, while the Ca-N distances fall in the range of 0.252 7(2)~0.262 4(2) nm.



Symmetry code:  $^i x-1/2, -y+3/2, z+1/2$ Fig.4 Molecular structure of **2**

Adjacent Ca (II) atoms are bridged by 2,2' -dithiosalicylate ligand, resulting in a one-dimensional infinite linear chain structure. In the chain, the adjacent Ca  $\cdots$  Ca distance is 1.162 9 nm (Fig.5). There exists intramolecular hydrogen bond among the free water molecule and carboxylate oxygen atom, with the O1W  $\cdots$  O2 distance of 0.288 0 (4) nm, and the O1W-H  $\cdots$  O2 bond angle of 131 (4) $^\circ$ , respectively. At the same time, there also exist intermolecular hydrogen bonds among the uncoordinated water molecules and coordinated carboxylate group. In addition, there are  $\pi \cdots \pi$  stacking interactions between adjacent phen molecules, with the Cg  $\cdots$  Cg (Cg is the centroid of the N-heterocycles) distance of 0.376 0 nm. As a sequence, a three-dimensional supramolecular network structure is constructed (as shown in Fig.6).

Symmetry code:  $^i x-1/2, -y+3/2, z+1/2$ Fig.5 1D chain structure of complex **2**Fig.6 Packing diagram of complex **2**

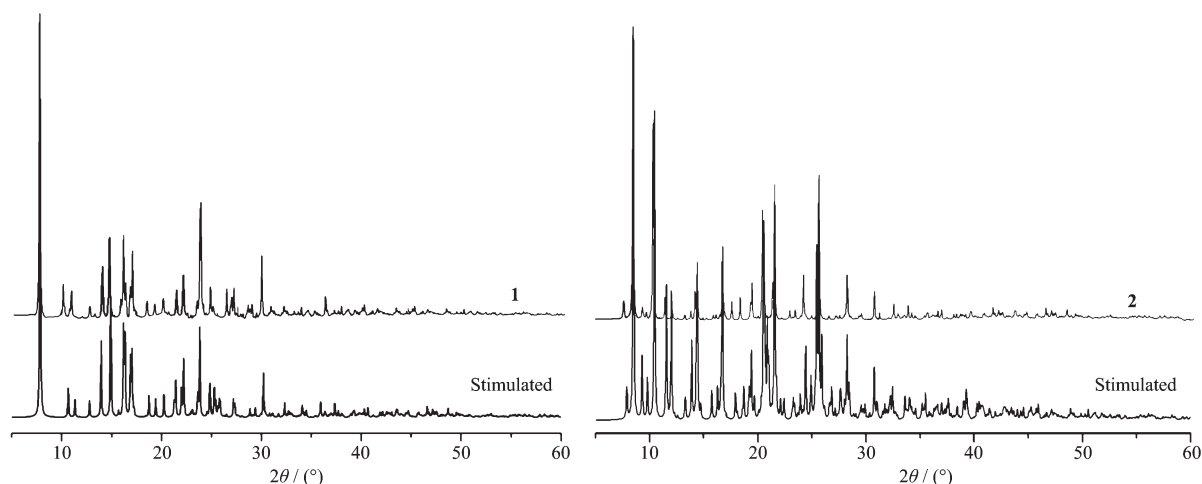
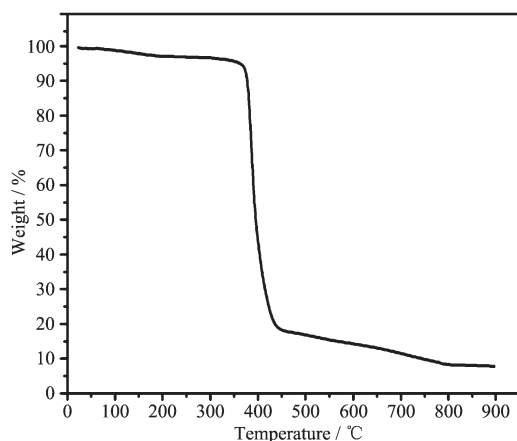
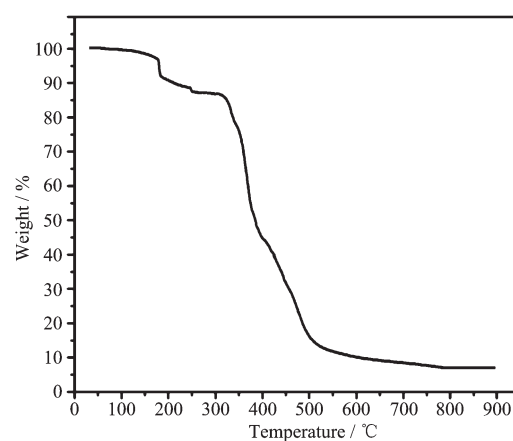
To the best of our knowledge, few complexes based on 2,2' -dithiosalicylate ligands have been structurally characterized to date, Such as three-fold interpenetrating three-dimensional coordination polymer<sup>[18]</sup>, [Cd (dtba) (bpp)]<sub>3n</sub> (H<sub>2</sub>dtba=2,2' -dithiosalicylic acid, bpp=1,3'-bis(4-pyridyl)propane), two-dimensional framework structure complexes, {[Cd<sub>2</sub> (dtba)<sub>2</sub> (1,4' -bix)<sub>2</sub>]  $\cdot$  3DMF}<sub>n</sub> and [Cd (dtba) (1,4' -btx)]<sub>n</sub> (1,4' -bix=1,4-bis(imidazol-1-ylmethyl)benzene, 1,4' -btx=1,4'-bis(triazol-1-ylmethyl)benzene), one-dimensional infinite chain structure complexes<sup>[19]</sup>, [Cd (Hdtba) (dtba)<sub>0.5</sub> (DMF)]<sub>n</sub> and {[Cd (dtba) (2,2' -bpy) (H<sub>2</sub>O)]  $\cdot$  2DMA}<sub>n</sub>. Obviously, diverse topological structures due to the differences in the bridging modes of 2,2' -dithiosalicylate ligand and the effect of the N-donor co-ligands.

### 2.3 PXRD and Thermogravimetric analysis

Powder X-ray diffraction (PXRD) patterns for solid samples of complexes **1** and **2** are measured at room temperature as illustrated in Fig.7. The patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding samples.

From the thermal analysis curves of complex **1** (Fig.8), we can see that there are three weight-loss steps. Above 27 up to 375  $^\circ\text{C}$ , a small amount of molecular fragment is found. A rapid weight loss can be detected from 375 to 458  $^\circ\text{C}$ , which is attributed to the dehydration of 2,2' -bipy molecule and phenyl group. After gradually burning decomposition, the final residue may be CuO (Found 8.32%, Calcd. 8.08%).

The result of TG analysis of the complex **2** is showed in Fig.9. The first weight loss can be detected from 37 to 178  $^\circ\text{C}$  (Found 4.99%, Calcd. 4.86%), which is attributed to the dehydration of the solvate water molecules. The weight loss occurring between 178 and 510  $^\circ\text{C}$  corresponds to decomposition of thiosalicylate group and phen molecule. The final residual is CaO (Found 7.28%, Calcd. 7.57%).

Fig.7 PXRD patterns for complexes **1** and **2**Fig.8 TG curve of complex **1**Fig.9 TG curve of complex **2**

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