2,2′-二硫代二苯甲酸、2,2′-二羧苯基硫醚及氮杂环配体的锌和钴配合物的合成、晶体结构与性质

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摘要：使用 2,2′-二硫代二苯甲酸和 1H-咪唑[4,5-f][1,10]菲咯啉(ip)、硝酸锌在水热条件下发生的原位反应合成了 1 个锌配合物，即[Zn(C$_{14}$H$_8$O$_4$S)(ip)(H$_2$O)] (**1**)(C$_{14}$H$_8$O$_4$S=2,2′-二羧苯基硫醚)；然后又利用 2,2′-二硫代二苯甲酸和咪唑(im)、硝酸钴在水溶液中合成了 1 个钴配合物，即 {[Co(C$_{14}$H$_8$O$_4$S$_2$)(im)$_2$]·H$_2$O}$_n$ (**2**)(C$_{14}$H$_8$O$_4$S$_2$=2,2′-二硫代二苯甲酸根)，并对它们分别进行了元素分析、红外光谱、热稳定性、荧光光谱、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，且锌原子是五配位的三角双锥结构。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，且钴原子是六配位的八面体结构。

关键词：2,2′-二硫代二苯甲酸；2,2′-二羧苯基硫醚；原位反应；晶体结构

Syntheses, Crystal Structures and Properties of Zinc(II) and Co(II) Complexes Constructed by 2,2′-Dithiosalicylic Acid, Bis(2-carboxyphenyl) Sulfide and N-Donor Ligands

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Abstract: The Zn(II) complex, [Zn(C$_{14}$H$_8$O$_4$S)(ip)(H$_2$O)]　(**1**) (C$_{14}$H$_8$O$_4$S=bis(2-carboxyphenyl) sulfide, ip=1H-imidazo[4,5-f][1,10]phenanthroline) was prepared with 2,2′-dithiosalicylic acid, ip and Zn(NO$_3$)$_2$·6H$_2$O by *in situ* hydrothermal reaction; while {[Co(C$_{14}$H$_8$O$_4$S$_2$)(im)$_2$]·H$_2$O}$_n$ (**2**) (C$_{14}$H$_8$O$_4$S$_2$=2,2′-dithiosalicylate, im=imidazole) was synthesized by mixing 2,2′-dithiosalicylic acid, im and cobalt dinitrate; after that they were characterized by elemental analysis, thermal analysis, IR, fluorescent spectra analysis, XRD and X-ray single crystal diffraction. Complex **1** has a dinuclear structure, and the Zn(II) ion is five-coordinated in a distorted trigonal bipyramidal geometry. Complex **2** has a one-dimensional chain structure, while the Co(II) ion is six-coordinated to form a distorted octahedral configuration. CCDC: 998515, **1**; 1002404, **2**.

Keywords: 2,2′-dithiosalicylic acid; bis(2-carboxyphenyl) sulfide; *in situ* reaction; crystal structure

0　Introduction

Recently, the design and synthesis of metal-organic supramolecular architectures have been well developed[1-5]. 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[6-10]. It has been proved that the utilization of appropriate

ligand as a connection is crucial to the construction of specific supramolecular structures. In general, the multiple coordination sites of the ligand incline towards forming higher dimensions[11-13]. The multifunctional thiodicarboxylic acid and its derivatives, which may link metal centers through both carboxylate groups and the S atom, are good candidates for the formation of different extended architectures[14]. 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 compl-exes[15]. Now, based on the use of thiodicarboxylate as a ligand, we have chosen 2,2′-dithiosalicylic 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 multi-functional 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[16]. In this context, we present the syntheses, crystal structures and the properties of the two complexes, namely [Zn(C$_{14}$H$_8$O$_4$S)(ip)(H$_2$O)] (**1**) and {[Co(C$_{14}$H$_8$O$_4$S$_2$)(im)$_2$]·H$_2$O}$_n$ (**2**), which incorporates 1*H*-imidazo[4,5-*f*][1,10]phenanthroline(ip) or imidazole(im) ligand.

1　Experimental

1.1　Reagent and instruments

All the regents 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 cm^{-1} (400~4 000 cm^{-1}). Thermogravimetry analyses were measured on a Perkin Elmer TG/DTA 6300 thermogravimetric analyzer under a flowing N$_2$ atmosphere with a heating rate of 10 ℃·min^{-1} starting at ambient temperature and heating up to 800 ℃,

using sample weight of 1~5 mg. Powder X-ray diffrac-tion (XRD) patterns were measured at 293 K on a Bruker D8 diffractometer (Cu *K*α, λ=0.154 059 nm, *U*=40 kV, *I*=10 mA), with the scanning speed of 0.2°·min^{-1}. The suitable single crystals of these complexes were employed for data collection on a Bruker P4 diffractometer with graphite monochromatized Mo *K*α (λ=0.071 073 nm).

1.2　Syntheses of the complexes

1.2.1　Synthesis of [Zn(C$_{14}$H$_8$O$_4$S)(ip)(H$_2$O)] (**1**)

The complex was prepared by the addition of ip (2.0 mmol), 2,2′-dithiosalicylic acid (2.0 mmol) and zinc nitrate hexahydrate (2.0 mmol) to a mixing solution of DMF (*N*,*N*-dimethylformamide), water and methanol (1:4:1, *V/V*, 20 mL). 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 colorless crystals were obtained from the filtered solution after several days. Analysis calculated for C$_{27}$H$_{18}$N$_4$O$_5$SZn(%): C 56.31, H 3.15, N 9.73; Found(%): C 56.30, H 3.16, N 9.74. IR (KBr, cm^{-1}): 3 392(w), 3 130(s), 3 040(s), 1 575(m), 1 500 (s), 1 392(m), 1 450(s), 1 388(s), 1 151(m), 1 036(s), 977(s), 876(s), 760(m), 480(s).

1.2.2　Synthesis of {[Co(C$_{14}$H$_8$O$_4$S$_2$)(im)$_2$]·H$_2$O}$_n$ (**2**)

2,2′-dithiosalicylic acid (2.0 mmol), cobalt nitrate hexahydrate (2.0 mmol) and im (2.0 mmol) were slowly added to a methanol and water solution (20 mL), and the pH value was adjusted to 7 with 0.1 mol·L^{-1} sodium hydroxide solution. The resulting solution was stirred for 45 min at room temperature, and then filtered. Red single crystals were obtained from the filtrate at room temperature for 7 days. Analysis calculated for C$_{20}$H$_{18}$N$_4$O$_5$S$_2$Co(%): C 46.42, H 3.51, N 10.83; Found(%): C 46.43, H 3.50, N 10.82%. IR (KBr, cm^{-1}): 3 560(s), 3 478(s), 3 418(w), 3 231(s), 1 640(s), 1 621(m), 1 596(s), 1 527(s), 1 383(m), 1 189(s), 1 069(m), 984(s), 740(m), 610(m), 479(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*α (λ=0.071 073 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. The C-H atoms were located and included at their geometrically idealized positions, with d_{C-H}= 0.093 nm and were refined as riding, with $U_{iso}(H)$= $1.2U_{eq}(C)$. The other hydrogen atoms of water molecules and N-H atoms were located in difference Fourier maps and refined in the riding model approximation,

with the O-H, H$\cdots$H and N-H distance restraints of 0.085(1), 0.139(1) and 0.090(1) nm, respectively, and with $U_{iso}(H)=1.5U_{eq}(O)$. All calculations were carried out with SHELXL 97 program[16]. The summary of the crystallographic data for the complexes are provided in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 998515, **1**; 1002404, **2**.

Table 1　Crystal data and structure parameters for the complexes

Complex	1	2
Formula	$C_{27}H_{18}N_4O_5SZn$	$C_{20}H_{18}N_4O_5S_2Co$
Formula weight	575.88	517.43
Temperature / K	296(2)	295(2)
Size / mm	0.30×0.20×0.18	0.36×0.28×0.20
θ range for data collection / (°)	2.54~25.00	1.70~25.00
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	1.077 1(6)	1.251 8(11)
b / nm	1.102 8(6)	2.274(2)
c / nm	1.137 7(6)	0.809 8(7)
α / (°)	64.142 0(10)	90
β / (°)	79.559 0(10)	106.440(10)
γ / (°)	79.559 0(10)	90
V / nm³	1.195 8(11)	2.211(3)
Z	2	4
D_c / (g·cm⁻³)	1.599	1.555
μ / mm⁻¹	1.163	1.005
$F(000)$	588	1 060
Reflections collected	7 486	12 125
Unique reflections (R_{int})	4 156 (0.017 2)	3 883 (0.025 8)
R, wR ($I>2\sigma(I)$)	0.026 4, 0.073 2	0.034 7, 0.767
R, wR (all data)	0.029 1, 0.075 2	0.042 9, 0.795
Goodness-of-fit (on F^2)	1.028	1.055
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm⁻³)	418, −191	307, −191

Table 2　Selected bond lengths (nm) and angles (°) for the complexes

Complex 1					
Zn(1)-O(1)	0.196 4(1)	Zn(1)-OW1	0.202 6(1)	Zn(1)-O(4)ⁱ	0.209 6(1)
Zn(1)-N(4)	0.209 9(1)	Zn(1)-N(3)	0.220 9(2)	S(1)-C(8)	0.178 1(2)
S(1)-C(7)	0.178 6(2)	O(1)-C(1)	0.127 0(2)	O(2)-C(1)	0.123 4(2)
O(3)-C(14)	0.124 3(2)	O(4)-C(14)	0.126 9(2)		
O(1)-Zn(1)-OW1	110.82(7)	O(1)-Zn(1)-O(4)ⁱ	98.52(6)	OW1-Zn(1)-O(4)ⁱ	91.66(6)
O(1)-Zn(1)-N(4)	131.35(6)	OW1-Zn(1)-N(4)	116.82(7)	O(4)ⁱ-Zn(1)-N(4)	89.62(6)

Continued Table 2

O(1)-Zn(1)-N(3)	96.47(6)	OW1-Zn(1)-N(3)	87.76(6)	O(4)i-Zn(1)-N(3)	164.15(6)
Complex **2**					
Co(1)-O(1)	0.205 8(2)	Co(1)-N(1)	0.208 1(3)	Co(1)-N(3)	0.210 4(3)
Co(1)-O1W	0.215 1(2)	Co(1)-O(4)i	0.218 4(2)	Co(1)-O(3)i	0.224 7(2)
S(1)-C(7)	0.180 3(3)	S(1)-S(2)	0.205 7(2)	S(2)-C(8)	0.178 4(3)
O(1)-C(1)	0.126 2(3)	O(2)-C(1)	0.124 1(3)	O(3)-C(14)	0.125 9(3)
O(4)-C(14)	0.126 9(3)				
O(1)-Co(1)-N(1)	102.64(9)	O(1)-Co(1)-N(3)	91.12(10)	N(1)-Co(1)-N(3)	92.59(10)
O(1)-Co(1)-O1W	91.85(9)	N(1)-Co(1)-O1W	90.95(9)	N(3)-Co(1)-O1W	174.78(8)
O(1)-Co(1)-O(4)i	95.31(9)	N(1)-Co(1)-O(4)i	161.52(8)	O1W-Co(1)-O(4)i	84.06(8)
O(1)-Co(1)-O(3)i	154.29(8)	N(3)-Co(1)-O(4)i	91.39(9)	N(1)-Co(1)-O(3)i	103.04(8)
N(3)-Co(1)-O(3)i	86.47(9)	O1W-Co(1)-O(3)i	89.00(8)	O(4)i-Co(1)-O(3)i	59.21(6)
C(7)-S(1)-S(2)	104.36(9)	C(8)-S(2)-S(1)	106.92(8)		

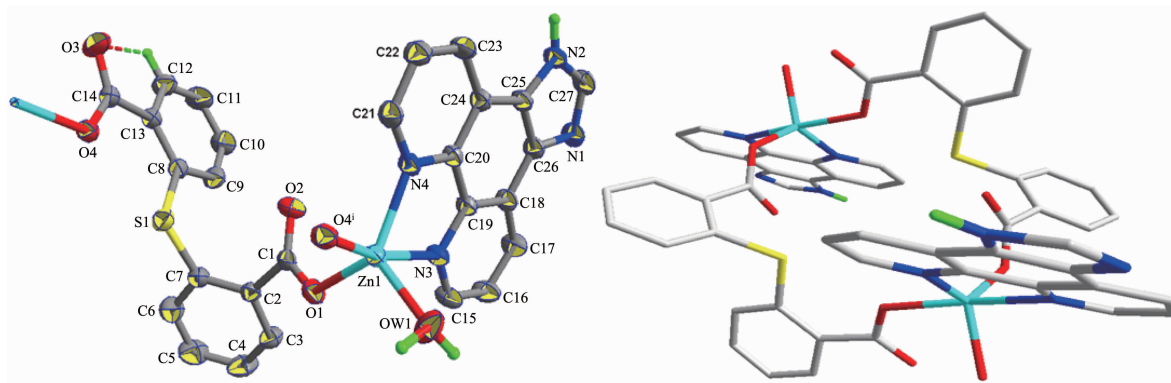Symmetry codes: i −x+1, −y+1, −z+1 for **1**; i x−1, y, z for **2**.

2 Results and discussion

2.1 Crystal structure of [Zn(C₁₄H₈O₄S)(ip)(H₂O)] (1)

The molecular structure of the complex **1** is depicted in Fig.1. The in situ reaction between 2,2′-dithiosalicylic acid, ip and zinc dinitrate offers the title Zn(Ⅱ) complex **1**, in which bis(2-carboxyphenyl) sulfide is generated. The carboxyl group is bound to the Zn(Ⅱ) atom in a monodentate coordination fashion via a single O atom, whereas the ip molecule acts as a bidentate chelating ligand coordinating through two N atoms. The X-ray diffraction analysis shows that this complex has a dinuclear structure. Each Zn(Ⅱ) ion lies on a distorted trigonal bipyramid with a ZnO₃N₂ chromophore, defined by two oxygen atoms from two different carboxyphenyl group and two N atoms from one ip co-ligand, as well as one water molecule. Atoms O1, OW1 and N4 comprise the equatorial plane, and O4i and N3 atoms occupy the apical sites (∠O(4)i-Zn(1)-N(3)=164.15(6)°; Symmetry codes: i −x+1, −y+1, −z+1). The Zn-N distances are 0.220 9(2) and 0.209 9(2) nm and the Zn-O bond lengths vary from 0.196 4(1) to 0.260 1(3) nm (Table 2).

Adjacent Zn(Ⅱ) ions are double-bridged by the bis(2-carboxyphenyl) sulfide ligand in the bis-monodentate mode, resulting in a dinuclear unit, generating a macrocyclic ring with the Zn⋯Zn separation distance of 0.854 6 nm (Fig.2). The dihedral angle between two benzene ring planes of bis(2-carboxyphenyl) sulfide ligand is 88.74(7)°, and the bond angle (∠C(8)-S(1)-C(7)) is 102.77(9)°. There is intramolecular hydrogen

Symmetry codes: i −x+1, −y+1, −z+1

Fig.1 Molecular structure of **1** with displacement ellipsoids drawn at the 30% probability level
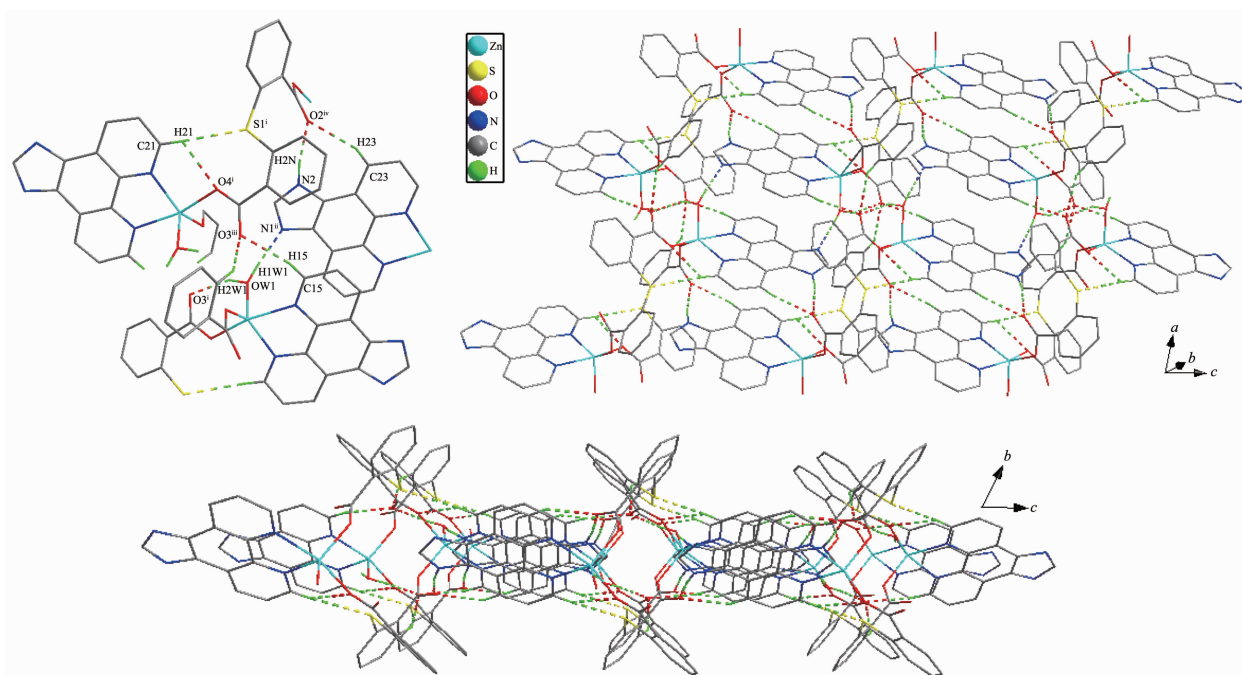
Symmetry codes: ^{i} $-x+1$, $-y+1$, $-z+1$; ^{ii} $-x$, $-y+1$, $-z$; ^{iii} $x-1$, y, z; ^{iv} $-x+1$, $-y+1$, $-z$

Fig.2   Two-dimensional structure of **1**

bond in the complex (C(12)−H(12)···O(3) 0.271 5(3) nm) (Fig.1, Table 3).

Additionally, there are five kinds of intramolecular hydrogen bonds: O−H···O (O(W1)−H(2W1)··· O(3)^i 0.264 4(2) nm), O−H···N (O(W1)−H(1W1)··· N(1)^{ii} 0.286 5(2) nm), N−H···O (N(2)−H(2N)···O(2)^{iv} 0.279 6(2) nm), C−H···O (C(3)−H(3)···O(3)^{iii} 0.324 4(3) nm, C(15)−H(15)···O(3)^{iii} 0.328 0(3) nm, C(23)−H(23) ···O(2)^{iv} 0.326 9(2) nm and C(21)−H(21)···O(4)^i 0.303 1(2) nm) and C−H···S (C(21)−H(21)···S(1)^i 0.364 4(2) nm) (Fig.2, Table 3). Such interactions of hydrogen bonds extend the binuclear units into a two-dimensional layer structure.

Furthermore, there exist π-π stacking interactions between adjacent two-dimensional sheet (C(22)− H(22)···Cg 0.346 8 nm, the centroid Cg is built by atoms C8, C9, C10, C11, C12 and C13), leading to the formation of a three-dimensional supramolecular network （Fig.3). By consideration that crystal packing results as the sum of many different contributions of directional and non-directional intermolecular interactions, it is important that different types of interactions are considered jointly in structure analysis, contributing to the stabilization of the crystal struc-
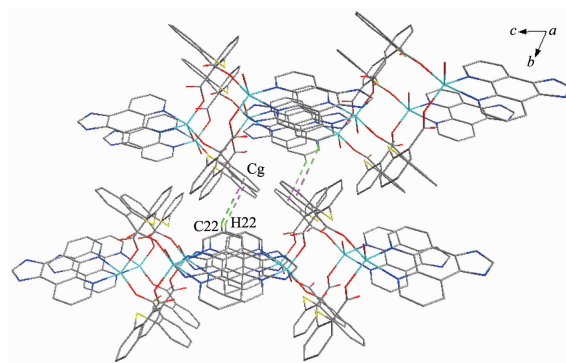

Fig.3   Three-dimensional structure of **1**

tures of the complexes.

2.2   Crystal structure of $\{[Co(C_{14}H_8O_4S_2)(im)_2]\cdot H_2O\}_n$ **(2)**

As depicted in Fig.4, the Co(Ⅱ) ion exists in a distorted octahedral coordination configuration, defined by two N-atom donors from two monodentate imidazole ligands, three O-atom donors from two different 2,2′-dithiosalicylate ligands, where one carboxylate group (O(3)-C(14)-O(4)) coordinates in a bidentate mode and the other group (O(1)-C(1)-O(2)) coordinates in a monodentate mode, as well as one coordination water molecule. Atoms O1, O3^i, O4^i and N1 comprise the equatorial plane, and atoms N3 and O1W occupy the axial positions (∠N(3)-Co(1)-O(1W)

Table 3 Hydrogen bond parameters for the complexes

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA / (°)
Complex **1**				
C(12)–H(12)⋯O(3)	0.093	0.238	0.271 5(3)	100.8
C(21)–H(21)⋯S(1)^i	0.093	0.272	0.364 4(2)	174.8
C(21)–H(21)⋯O(4)^i	0.093	0.248	0.303 1(2)	118.4
O(W1)–H(2W1)⋯O(3)^i	0.083 7(9)	0.188(1)	0.264 4(2)	151(2)
O(W1)–H(1W1)⋯N(1)^{ii}	0.084 7(9)	0.202(1)	0.286 5(2)	173(2)
C(3)–H(3)⋯O(3)^{iii}	0.093	0.243	0.324 4(3)	146.0
C(15)–H(15)⋯O(3)^{iii}	0.093	0.237	0.328 0(3)	166.5
N(2)–H(2N)⋯O(2)^{iv}	0.090 3(17)	0.192(2)	0.279 6(2)	165(2)
C(23)–H(23)⋯O(2)^{iv}	0.093	0.241	0.326 9(2)	154.0
Complex **2**				
O(1W)–H(1W1)⋯O(2)	0.084(3)	0.179(3)	0.260 0(3)	160(3)
C(3)–H(3)⋯O(1)	0.093	0.246	0.278 3(4)	100.2
C(6)–H(6)⋯S(2)	0.093	0.262	0.315 9(4)	117.8
C(9)–H(9)⋯S(1)	0.093	0.266	0.320 3(4)	117.7
C(12)–H(12)⋯O(4)	0.093	0.245	0.278 0(4)	100.6
O(1W)–H(2W1)⋯O(3)^{iii}	0.079(3)	0.202(3)	0.280 3(3)	172(3)
N(2)–H(2N)⋯O(4)^{iv}	0.086	0.237	0.306 6(4)	138.0
N(4)–H(4N)⋯O(4)^v	0.086	0.200	0.280 8(4)	156.0
C(11)–H(11)⋯S(2)^{vi}	0.093	0.273	0.360 6(4)	158.4

Symmetry codes: ^{i} −x+1, −y+1, −z+1, ^{ii} −x, −y+1, −z, ^{iii} x−1, y, z, ^{iv} −x+1, −y+1, −z for **1**; ^{iii} −x+1, −y+1, −z+1, −z, ^{iv} x−1, y, z+1, ^{v} x−1, −y+1/2, z+1/2, ^{vi} x, y, z−1 for **2**.

= 174.78(8)°; Symmetry codes: ^{i} x−1, y, z). The Co-O distances fall in the range of 0.205 8(2)~0.224 7(2) nm, while the Co-N distances fall in the range of 0.252 7(2) ~0.209 6(1) nm. The dihedral angles between two imidazoles as well as between two benzene ring planes of the 2,2′-dithiosalicylate ligand are 84.189 (104)° and 85.532(139)°, respectively. The difference for torsion angle C(7)-S(1)-S(2)-C(8), 82.55(12)°, may be attributed to the remarkable conformational flexibility
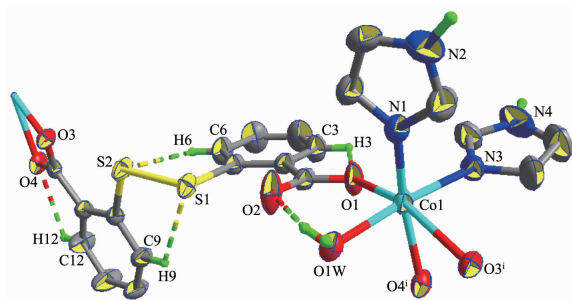

Symmetry codes: ^{i} x−1, y, z

Fig.4 Molecular structure of **2** with displacement ellipsoids drawn at the 30% probability level

of 2,2′-dithiosalicylate ligand. Three kinds of intra-molecular hydrogen bonds are observed in the complex: O−H⋯O (O(1W)−H(1W1)⋯O(1) 0.278 3(4) nm), C−H⋯O (C(3)−H(3)⋯O(1) 0.278 3(4) nm, C(12) −H(12)⋯O(4) 0.278 0(4) nm and C−H⋯S (C(6)− H(6)⋯S(2) 0.315 9(4) nm and C(9)−H(9)⋯S(1) 0.320 3(4) nm), as shown in Table 3.

Adjacent Co(Ⅱ) ions are bridged by 2,2′-dithiosalicylate ligand, which adopts a tridentate coordination mode, resulting in a one-dimensional infinite chain structure. In the chain, the adjacent Co⋯Co distance is 1.251 8 nm (Fig.5). Interestingly, it is observed that there exists two kinds of intermolecular hydrogen bond: N−H⋯O (N(2)−H(2N)⋯O(4)^{iv} 0.306 6(4) nm and N(4)−H(4N)⋯O(4)^v 0.280 8(4) nm) and C−H⋯S (C(11)−H(11)⋯S(2)^{vi} 0.360 6(4) nm), resulting in the two-dimensional layer structure (Fig.5 and Table 3, Symmetry codes: ^{iv} x−1, y, z+1; ^{v} x−1, −y +1/2, z+1/2; ^{vi} x, y, z−1).

In addition, there also exist other intermolecular

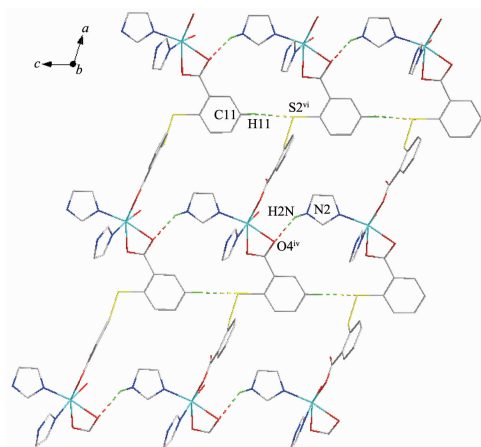Fig.5　Two-dimensional layer structure of complex **2**

Fig.6　Three-dimensional structure of complex **2**

hydrogen bond $(O(1W)-H(2W1)\cdots O(3)^{iii}\ 0.280\ 3(3)$ nm, Symmetry codes: ^{ii} $-x+1$, $-y+1$, $-z+1$). As a sequence, a three-dimensional supramolecular network structure is constructed (Fig.6, Table 3).

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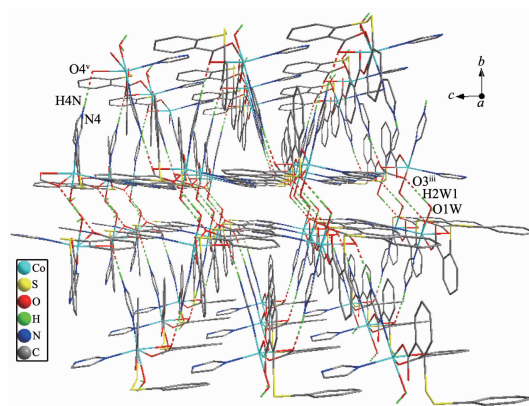
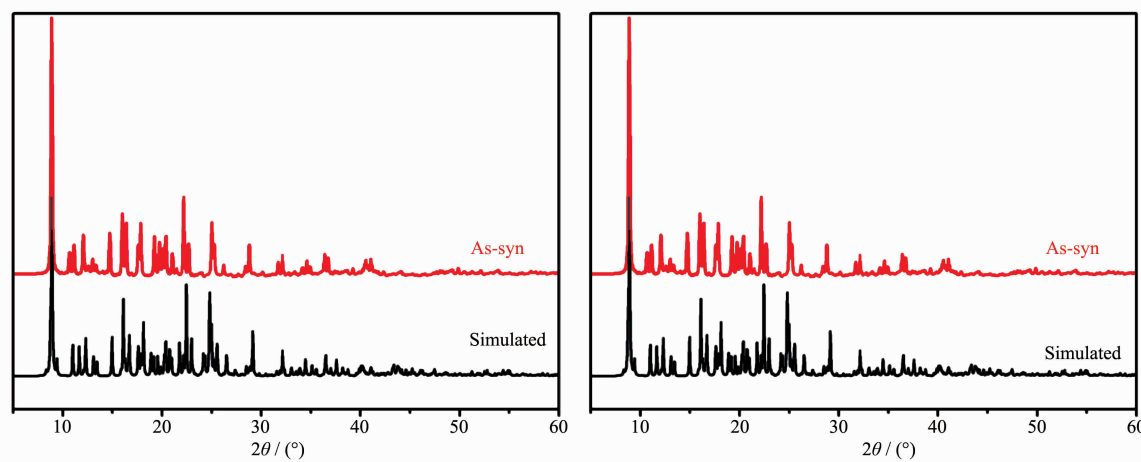　　Powder X-ray diffraction (XRD) patterns for solid samples of complexes **1** and **2** are measured at room temperature as illustrated in Fig.7. The patterns are highly similar to their simulated ones　(based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures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

Fig.7　XRD patterns for complexes **1** and **2**

　　From the thermal analysis curves of complex **1** (Fig.8), we can see that there are three weight-loss steps. Above 40 ℃ up to 253 ℃, a small weight loss is found (Found 3.03%, Calcd. 3.13%), which is attributed to the dehydration of the coordinated water molecules.. A rapid weight loss can be detected from 253 to 516 ℃, which is attributed to the dehydration of ip molecules and phenyl groups. After gradually burning decomposition, the final residue may be ZnO (Found 14.28%, Calcd. 14.13%).

　　The result of TG analysis of the complex **2** is
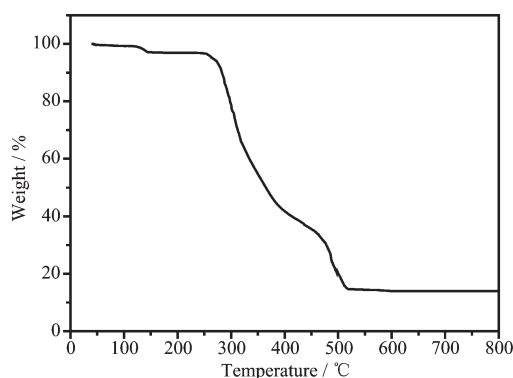
Fig.8　TG curve of complex **1**

showed in Fig.9. The first weight loss can be detected from 50 to 250 ℃ (Found 3.45%, Calcd. 3.48%), which is attributed to the dehydration of the coordinated water molecules. The weight loss occurring between 250 and 515 ℃ corresponds to decomposition of imidazoles molecules and phen molecules. The final residual is CoO (Found 14.23%, Calcd. 14.48%).
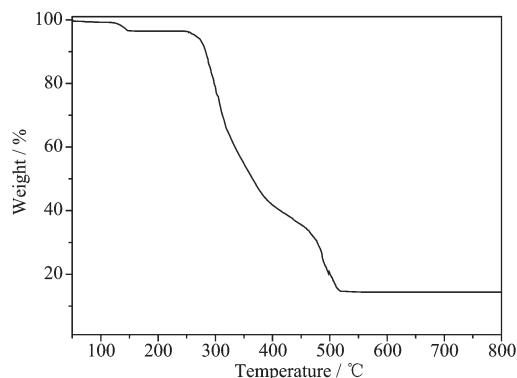

Fig.9 TG curve of complex **2**

2.4 Fluorescent spectra analysis

The free ip ligand shows strong emission peak centered at 460 nm upon excitation at 315 nm, but the free bis(2-carboxyphenyl) sulfide ligand didn′t
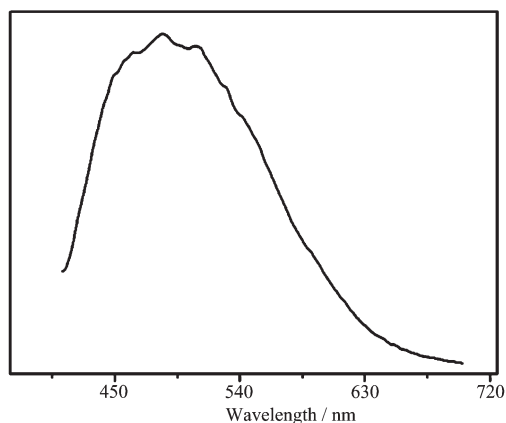

Fig.10 Emission spectrum of **1** in the solid state at room temperature

show the emission peak. Excitation (λ_{ex}=395 nm) of the complex **1** in the solid state at room temperature produces fluorescent emissions at 483 nm (Fig.10). It may originate from the emission of free ip ligand.

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