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刚性配体 1,3,5-三(1-咪唑基)苯与 1,2,4-苯三甲酸构筑的金属配合物:水热合成及晶体结构

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摘要:由水热法合成了 2 个配合物[Co(1,2,4-HBTC)(tib)] (**1**)和[Ni_4(1,2,4-$BTC)_2$(tib)$_4$($H_2O)_2$]·(1,2,4-HBTC)·9H_2O (**2**) (1,2,4-H_3BTC=1,2,4-苯三甲酸,tib=1,3,5-三(1-咪唑基)苯),并用元素分析、红外光谱、X-射线单晶衍射及热重分析等对其进行了表征。晶体结构分析结果表明:配合物 **1** 是由 Co(Ⅱ)和 tib 连接形成的二维层状结构,1,2,4-$HBTC^{2-}$作为端基配体与 Co(Ⅱ)配位,而配合物 **2** 是通过 1,2,4-BTC^{3-}连接[Ni(tib)]$^{2+}$二维网形成最终的二维多层结构,这 2 个化合物最终均被氢键连接形成三维超分子结构。

关键词:1,2,4-苯三甲酸;1,3,5-三(1-咪唑基)苯;晶体结构;水热合成
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Hydrothermal Syntheses and Crystal Structures of Two Metal Complexes with Mixed 1,2,4-Benzenetricarboxylic Acid and 1,3,5-Tris(1-imidazolyl)benzene Ligands

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Abstract: Two new coordination complexes [Co(1,2,4-HBTC)(tib)] (**1**) and [Ni_4(1,2,4-$BTC)_2$(tib)$_4$($H_2O)_2$]·(1,2,4-HBTC)·9H_2O (**2**) (1,2,4-H_3BTC=1,2,4-benzenetricarboxylic acid, tib=1,3,5-tris(1-imidazolyl)benzene) were obtained by hydrothermal reactions of 1,2,4-H_3BTC and tib with corresponding metal salts. Single crystal X-ray diffraction analysis revealed that each tib ligands connect three metal atoms to form two-dimensional (2D) networks in **1** and **2**. On the other hand, each 1,2,4-$HBTC^{2-}$ coordinates to one Co(Ⅱ) atom as a terminal ligand in **1**, while in **2**, two 1,2,4-BTC^{3-} ligands link four Ni(Ⅱ) atoms which further connect [Ni(tib)]$^{2+}$ 2D networks to result in formation of multi-layered 2D structure. Complexes **1** and **2** are finally extended to three-dimensional (3D) supramolecular structures by hydrogen bonding interactions. CCDC: 816549, **1**; 815931, **2**.

Key words: 1,2,4-benzenetricarboxylic acid; 1,3,5-tris(1-imidazolyl)benzene acid; crystal structure; hydrothermal synthesis

In recent years, the design and synthesis of metal-organic frameworks (MOFs) constructed from metal salts and bridging organic ligands have attracted great attention, not only because of their intriguing variety of architectures and topologies[1-5], but also because of their potential applications in ion-exchange, nonlinear optics, gas storage, catalysis, magnetism and molecular sensing[6-10]. Consequently, a variety of MOFs with inter-

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esting structures and topologies have been prepared by taking certain factors into account, for example the coordination nature of the metal ion and the shape, functionality, flexibility of organic ligand and so on[11-12]. From the viewpoint of crystal engineering, the most effective approach may be the appropriate choice of well-designed organic ligands containing modifiable backbones and connectivity, together with the metal centers with definite coordination preferences[13-15]. On the other hand, mixed ligands with different donor groups have been proved to be effective building units to construct novel coordination polymers, because they have strong coordination affinity and can satisfy the geometric need of metal centers[16-19]. According to the above consideration and to further investigate the influence of organic ligands on the coordination architectures, reactions of varied metal salts with 1,2,4-benzenetricarboxylic acid and 1,3,5-tris (1-imidazolyl) benzene mixed ligands were carried out. Herein we report the synthesis, crystal structure and thermogravimetric analysis of two coordination polymers, [Co (1,2,4-HBTC) (tib)] (**1**) and [Ni_4 (1,2,4-BTC)$_2$ (tib)$_4$ (H_2O)$_2$] · (1,2,4-HBTC) · 9H_2O (**2**) (1,2,4-H_3BTC = 1,2,4-benzenetricarboxylic acid, tib = 1,3,5-tris (1-imidazolyl) benzene).

1 Experimental

1.1 Materials and instruments

The regents and solvents were used as commercial sources without further purification. The tib ligand was prepared according to the method reported previously[20]. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on Bruker Vector22 FTIR spectrophotometer using KBr discs. Thermogravimetric analyses (TGA) were performed on a TGA V5.1A Dupont 2100 instrument heating from room temperature to 700 ℃ under N_2 with a heating rate of 20 ℃ · min^{-1}.

1.2 Syntheses of the compounds 1 and 2

Complex **1** was synthesized by hydrothermal method in a 16 mL Teflon-lined autoclave by heating a mixture containing $Co(ClO_4)_2 \cdot 6H_2O$ (73.1 mg, 0.2 mmol), 1,2,4-H_3BTC (21.2 mg, 0.1 mmol), tib (27.3 mg, 0.1 mmol) and NaOH (12.0 mg, 0.3 mmol) in 10 mL H_2O at 180 ℃ for 3 d. Violet block single crystals of **1** were collected with a yield of 42% by filtration and washed by water and ethanol for several times. Anal. Calcd. for $C_{24}H_{16}CoN_6O_6$(%): C, 53.00; H, 2.94; N, 15.46. Found(%): C, 53.08; H, 2.89; N, 15.49%. IR (KBr pellet, cm^{-1}): 3 410(s, br), 1 721(s), 1 621(s), 1 598 (s), 1 513(m), 1 377(m), 1 324(w), 1 256(m), 1 233(m), 1 105(s), 1 016(m), 950(m), 744(m), 684(w), 651(m), 622(m).

The preparation of **2** is similar to that of **1** except that $Ni(ClO_4)_2 \cdot 6H_2O$ (75.1 mg, 0.2 mmol), instead of $Co(ClO_4)_2 \cdot 6H_2O$, was used. Blue block crystals of **2** were obtained in 34% yield after washing by water and ethanol for several times. Anal. Calcd. for $C_{87}H_{80}N_{24}Ni_4O_{29}$(%): C, 48.32; H, 3.70; N, 15.55. Found(%): C, 48.12; H 3.64; N, 15.69. IR (KBr pellet, cm^{-1}): 3 410(s, br), 1 720(s), 1 618(s), 1 572(s), 1 515(s), 1 394(s), 1 318 (m), 1 243(s), 1 110(m), 1 074(s), 1 018(m), 950(m), 854 (m), 763(m), 749(m), 650(m).

1.3 Structure determination

The crystallographic data collections for complexes **1** and **2** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 075 nm) at 200 K using the ω-scan technique. The structures were solved by direct methods using SIR92 and expanded using Fourier techniques[21-22]. All non-hydrogen atoms were refined anisotropically. All calculations were performed using the Crystal Structure (Version 3.8) crystallographic software package except for the refinement, which was performed using SHELXL-97[23-24]. Hydrogen atoms of the ligands tib and 1,2,4-BTC^{3-} in the structures were generated geometrically. The hydrogen atom of non-deprotonated 1,2,4-$HBTC^{2-}$ was located directly in **1** (H1), and was not found in **2**. The hydrogen atoms of water molecules in **2** were also not found except for O11 and O12 with attached hydrogen atoms found in the differential Fourier map and located. Each atom of C311, C322, O7, O8, O9 and O10 in **2** has the site occupancy factors of 0.75. And atom O15 has site occupancy of 0.5 and O16 in **2** was disordered into two positions with the site occupancy factors of

0.60(3) and 0.40(3), respectively. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

CCDC: 816549, **1**; 815931, **2**.

Table 1　Crystal data and structure parameters for complexes 1 and 2

Complexes	**1**	**2**
Empirical formula	$C_{24}H_{16}N_6CoO_6$	$C_{87}H_{80}N_{24}Ni_4O_{29}$
Formula weight	543.36	2 160.53
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	0.777 0(3)	1.025 5((2)
b / nm	1.809 7(7)	1.136 6(2)
c / nm	1.568 1(6)	1.996 9(5)
α / (°)	90	93.026(8)
β / (°)	106.010(14)	102.453(9)
γ / (°)	90	105.891(7)
V / nm^3	2.119 4(14)	2.170 4(9)
Z	4	1
Absorption coefficient / mm^{-1}	0.87	0.956
F(000)	1 108	1 114
Reflections collected / unique (R_{int})	18 447 / 4 673 (0.127 4)	20 327 / 9 751 (0.117 1)
Data / restraints / parameters	4 673 /0 / 338	9 751 / 91 / 683
Final R indices ($I>2\sigma(I)$)	R_1=0.050 9, wR_2=0.118 1	R_1=0.062 3, wR_2=0.172 3
Largest diff. peak and hole / (e·nm^{-3})	680, −830	1 210, −930

Table 2　Selected bond lengths (nm) and bond angles (°)

		1			
Co(1)-O(5)	0.232 1(2)	Co(1)-O(6)	0.203 5(2)	Co(1)-N(32)$^{\#2}$	0.202 6(2)
Co(1)-N(12)	0.203 6(2)	Co(1)-N(52)$^{\#1}$	0.205 1(2)		
N(32)$^{\#2}$-Co(1)-N(12)	110.46(9)	N(12)-Co(1)-O(5)	88.56(9)	O(6)-Co(1)-O(5)	60.07(8)
O(6)-Co(1)-N(12)	113.06(9)	N(32)$^{\#2}$-Co(1)-O(6)	123.88(8)	N(52)$^{\#1}$-Co(1)-O(5)	153.18(8)
O(6)-Co(1)-N(52)$^{\#1}$	93.84(9)	N(32)$^{\#2}$-Co(1)-N(52)$^{\#1}$	114.05(9)		
N(32)$^{\#2}$-Co(1)-O(5)	87.92(8)	N(12)-Co(1)-N(52)$^{\#1}$	97.19(9)		
		2			
Ni(1)-O(1)	0.215 3(4)	Ni(1)-N(52)$^{\#1}$	0.206 2(4)	Ni(2)-O(6)	0.212 5(4)
Ni(1)-O(2)	0.217 9(4)	Ni(1)-N(32)$^{\#2}$	0.205 2(3)	Ni(2)-N(112)	0.208 7(3)
Ni(1)-O(3)$^{\#5}$	0.206 4(4)	Ni(2)-O(11)	0.203 2(5)	Ni(2)-N(152)$^{\#3}$	0.205 2(4)
Ni(1)-N(12)	0.204 8(3)	Ni(2)-O(5)	0.217 7(4)	Ni(2)-N(132)$^{\#4}$	0.207 1(3)
O(1)-Ni(1)-O(2)	60.94(12)	O(11)-Ni(2)-O(6)	103.62(15)	N(52)$^{\#1}$-Ni(1)-O(1)	96.82(14)
O(3)$^{\#5}$-Ni(1)-O(2)	104.32(12)	O(11)-Ni(2)-N(132)$^{\#4}$	88.95(15)	N(32)$^{\#2}$-Ni(1)-O(2)	89.89(12)
O(3)$^{\#5}$-Ni(1)-O(1)	164.93(12)	N(152)$^{\#3}$-Ni(2)-N(132)$^{\#4}$	85.90(13)	N(112)-Ni(2)-O(5)	88.51(14)
N(12)-Ni(1)-O(3)$^{\#5}$	95.59(13)	N(152)$^{\#3}$-Ni(2)-O(6)	160.20(15)	N(152)$^{\#3}$-Ni(2)-O(5)	98.67(15)
N(52)$^{\#1}$-Ni(1)-O(3)$^{\#5}$	97.59(14)	N(132)$^{\#4}$-Ni(2)-N(112)	177.47(17)	O(11)-Ni(2)-O(5)	165.04(14)
N(32)$^{\#2}$-Ni(1)-O(1)	91.62(13)	N(12)-Ni(1)-N(32)$^{\#2}$	178.58(14)	O(11)-Ni(2)-N(152)$^{\#3}$	96.18(17)
N(12)-Ni(1)-O(2)	88.69(12)	N(12)-Ni(1)-N(52)$^{\#1}$	94.76(12)	O(11)-Ni(2)-N(112)	88.53(15)

Continued Table 2

N(52)$^{\#1}$-Ni(1)-O(2)	157.39(15)	N(32)$^{\#2}$-Ni(1)-N(52)$^{\#1}$	86.52(13)	N(152)$^{\#3}$-Ni(2)-N(112)	94.62(13)
N(132)$^{\#4}$-Ni(2)-O(5)	93.86(14)	N(32)$^{\#2}$-Ni(1)-O(3)$^{\#5}$	84.85(13)	N(112)-Ni(2)-O(6)	86.30(13)
O(6)-Ni(2)-O(5)	61.55(12)	N(12)-Ni(1)-O(1)	87.61(13)	N(132)$^{\#4}$-Ni(2)-O(6)	94.04(12)

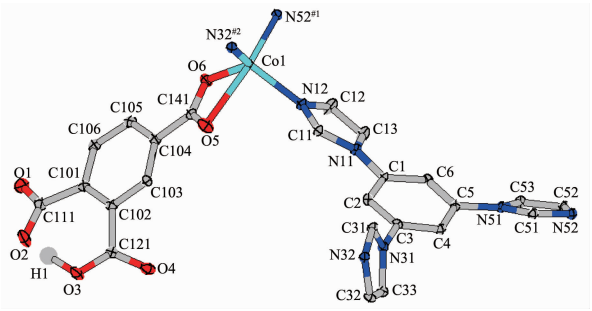
Symmetry codes: **1**: $^{\#1}$ −1+x, 3/2−y, −1/2+z; $^{\#2}$ 1−x, 1−y, 1−z; **2**: $^{\#1}$ x, 1+y, z; $^{\#2}$ 1+x, 1+y, z; $^{\#3}$ 1+x, −1+y, z; $^{\#4}$ −1+x, −1+y, z, $^{\#5}$ 1−x, 1−y, 2−z.

2 Results and discussion

2.1 Crystal structure description

The results of structural analysis revealed that complex **1** has a two-dimensional (2D) layer structure. The asymmetric unit of **1** contains one Co (II) atom, one tib and one partially deprotonated 1,2,4-HBTC^{2-} ligand. The presence of non-deprotonated carboxylic group (-COOH) of 1,2,4-HBTC^{2-} in **1** was also confirmed by IR spectral data (vide post). As shown in Fig.1, the central Co(Ⅱ) atom has distorted square-pyramidal coordination environment as indicated by an index τ value of 0.49[25] and is coordinated by two oxygen and two nitrogen atoms (O5, O6, N52$^{\#1}$ and N32$^{\#2}$) in the equatorial plane and the other nitrogen atom (N12) in the axial position. Two Co-O bond distances are 0.232 1(2), 0.203 5(2) nm and three Co-N ones are 0.202 6(2), 0.203 6(2) and 0.205 1(2) nm, respectively (Table 2). On the other hand, each tib ligand acts as a three-connector to link three Co (Ⅱ) atoms to form a 2D network with (4,8^2) topology (Fig.2). It is noteworthy that each 1,2,4-HBTC^{2-} uses only one carboxylate group to coordinate with one Co (Ⅱ) atom as a terminal ligand. Thus the final structure of **1** is a 2D network as exhibited in Fig.2.

When $Ni(ClO_4)_2\cdot 6H_2O$ was used, instead of $Co(ClO_4)_2\cdot 6H_2O$, to react with ligand tib and 1,2,4-



Hydrogen atoms are omitted for clarity except the one (H1) of non-deprotonated carboxylic acid

Fig.1 Coordination environment of Co(Ⅱ) in **1** with ellipsoids drawn at the 30% probability level

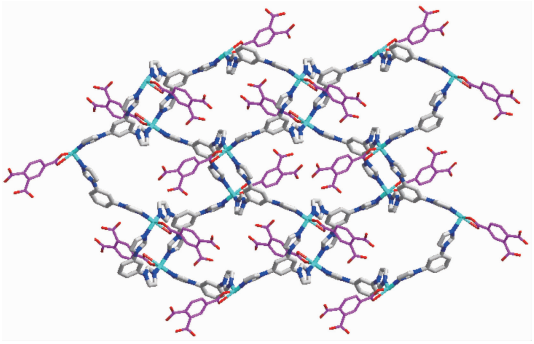
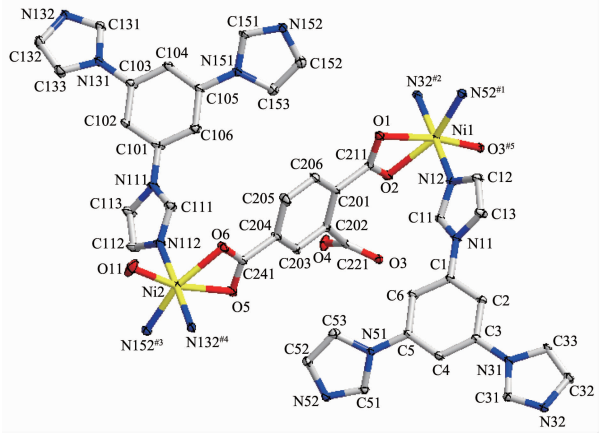


Fig.2 2D network of **1** with all hydrogen atoms omitted for clarity

H_3BTC, complex **2** with different 2D structure was obtained. The asymmetric unit of **2** contains two Ni(Ⅱ) atoms, two tib, one coordinated 1,2,4-BTC^{3-} and half non-coordinated 1,2,4-HBTC^{2-}, one coordinated and four and half free water molecules. The coordination environment of Ni(Ⅱ) in **2** is shown in Fig.3. It can be seen that both Ni(1) and Ni(2) have similar distorted octahedral coordination environments, which is obviously different from the distorted square-pyramidal Co(Ⅱ) in **1**. Each Ni(1) atom is coordinated by three nitrogen (N12, N52$^{\#1}$ and N32$^{\#2}$) atoms from three different tib ligands and three carboxylate oxygen (O1, O2 and O3$^{\#5}$) atoms from two distinct 1,2,4-BTC^{3-}



Free water molecules, non-coordinated 1,2,4-HBTC^{2-} and hydrogen atoms are omitted for clarity

Fig.3 Coordination environment of Ni(Ⅱ) in **2** with ellipsoids drawn at the 30% probability level

ligands, while Ni(2) is coordinated by three nitrogen (N112, N152$^{\#3}$ and N132$^{\#4}$) atoms from three different tib ligands and two carboxylate oxygen (O5, O6) atoms from one 1,2,4-BTC^{3-} and one oxygen atom (O11) from a terminal water molecule with Ni-N bond lengths ranging from 0.204 8(3) to 0.208 7(3) nm, the Ni-O ones in the range of 0.203 2(5)~0.217 9(4) nm and bond angles around the Ni(Ⅱ) in the range of 60.94 (12)° to 178.58(14)° (Table 2). It is interesting to find that each tib ligand coordinates to three Ni(Ⅱ) atoms, however, leading to the formation of typical 6^3-hcb 2D network (Fig.4), rather than the $(4,8^2)$ one in **1**. Furthermore, the coordination mode of 1,2,4-BTC^{3-} ligand in **2** is completely different from that in **1**. Each 1,2,4-BTC^{3-} in **2** connects three Ni(Ⅱ) atoms using its three carboxylate groups, and two 1,2,4-BTC^{3-} ligands and four Ni(Ⅱ) atoms form a Ni_4 $(1,2,4\text{-BTC})_2$ subunit which further links adjacent four Ni-tib 2D networks to result in formation of a multi-layered 2D structure of **2** (Fig.4). The non-coordinated 1,2,4-HBTC^{2-} and water molecules are located between the two adjacent 2D layers.

Both 2D networks of **1** and **2** are further connected together through hydrogen bonding interactions (Table 3) to give the corresponding three-dimensional (3D) supramolecular structures. The different structures of complexes **1** and **2** imply that the metal centers play crucial role in the formation of the frameworks **1** and **2**.

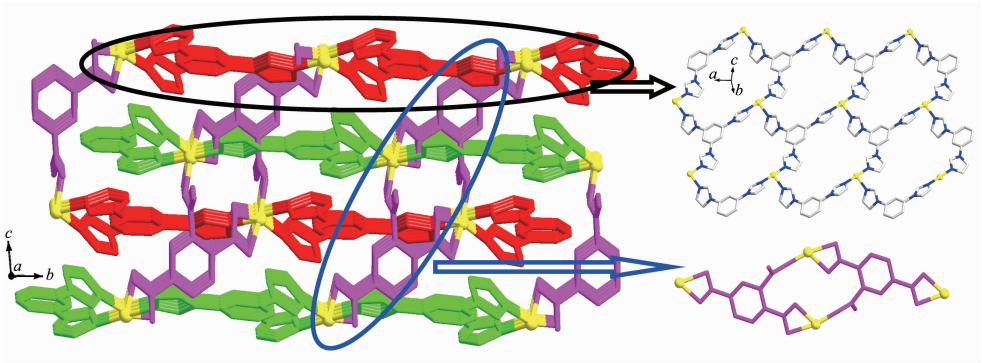


Fig.4　2D structure of **2**

Table 3　Hydrogen bonding data for complexes 1 and 2

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A)/ nm	∠D-H-A / (°)
1				
C2–H2···O2#1	0.095	0.249	0.333 5(4)	148
C4–H3···O4#2	0.095	0.231	0.308 8(4)	139
C13–H7···O4#3	0.095	0.250	0.333 4(4)	147
C31–H8···O1#4	0.095	0.234	0.327 1(4)	166
C33–H10···O1#3	0.095	0.252	0.336 5(4)	149
C51–H11···O4#2	0.095	0.233	0.323 5(4)	159
2				
C11–H4···O3	0.095	0.234	0.328 8(6)	177
C31–H7···O12#1	0.095	0.252	0.331 8(6)	141
C51–H10···O4#2	0.095	0.236	0.317 7(6)	143
C104–H14···O13#3	0.095	0.257	0.3514(6)	172
C131–H19···O13#3	0.095	0.256	0.334 8(6)	141
C132–H20···O7#4	0.095	0.260	0.333(2)	134
C133–H21···O16#4	0.095	0.229	0.323 5(15)	175
O11–H101···O14#5	0.084	0.194	0.276 7(9)	169
O11–H102···O9	0.084	0.234	0.316 5(9)	169
O12–H104···O4#6	0.083	0.212	0.293 1(6)	166

Symmetry transformation used to generate equivalent atoms for **1**: $^{\#1}$ x, 1/2−y, 1/2+z; $^{\#2}$ 2−x, 1−y, 1−z; $^{\#3}$ 2−x, 1/2+y, 1/2−z; $^{\#4}$ 1−x, 1/2+y, 1/2−z; for **2**: $^{\#1}$ 1+x, −1+y, z; $^{\#2}$ 1−x, −y, 2−z; $^{\#3}$ 2−x, 1−y, 1−z; $^{\#4}$ 1+x, y, z; $^{\#5}$ 1−x, −y, 1−z; $^{\#6}$ 2−x, 1−y, 2−z.

2.2 IR and thermogravimetric analyses

The infrared spectra (IR) of the complexes **1** and **2** have been recorded and strong IR bands from -COOH were observed at 1 721 and 1 720 cm^{-1}, respectively, indicating the non-complete deprotonation of 1,2,4-H_3BTC in **1** and **2**, which is coincident with the results of crystallographic structural analysis. On the other hand, the thermogravimetric analyses (TGA) of compounds **1** and **2** were performed and the results are shown in Fig.5. For complex **1**, no obvious weight loss was observed before 350 ℃, and above this temperature, the structure decomposed due to the liberation of the organic ligands. For complex **2**, the first weight loss of 10.0% between 25 and 215 ℃ indicates the loss of free and coordinated water molecules (calcd. 9.17%), and the residue remains unchanged until about 340 °C, then a rapid weight loss was detected, which is attributed to the decomposition of the complex.

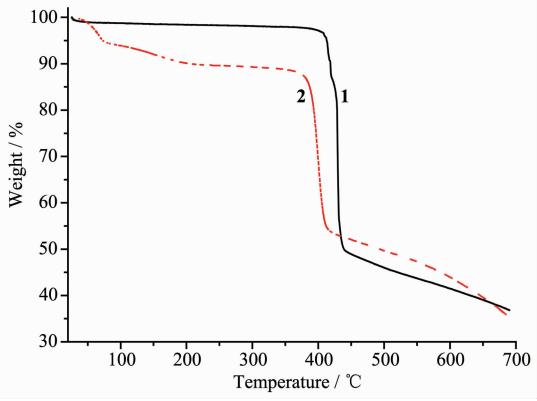


Fig.5 TG curves of compounds **1** and **2**

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