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## Thermostable and Insensitivity Furazan Energetic Complexes:

## Syntheses, Structures and Modified Combustion Performance

## for Ammonium Perchlorate

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### Abstract

CC

It is an important issue to balance energy and sensitivity in the construction of high materials. furozacycline energy Herein, two energetic complexes  $([Zn(HTZF)(H_2O)_3] \cdot H_2O$  $[Co(HTZF)(H_2O)_3] \cdot 2H_2O \quad (2)$ (HTZF (1) and 3-hydroxyl-4-(tetrazol-5-yl) furazan)) were hydrothermally synthesized. Single crystal X-ray diffraction shows that in **1**, energetic ligand adopting bidentate chelating coordination mode coordinates to  $Zn^{2+}$ . The coordinated units  $Zn(HTZF)_2(H_2O)_2$  and  $Zn(H_2O)_4$  are alternatively linked to an infinite chain through nitrogen atom in furazan group, and with the aid of hydrogen bonding interaction, forming 3D supramolecule structure. Different in 2, ligand coordinates to  $Co^{2+}$  in bidentate chelating coordination and bridging coordination modes.  $\pi \cdots \pi$  interaction further supports 3D framework stabilization. The thermal decomposition temperature of 1 and 2 are up to 293.0 °C and 295.8 °C, respectively. The heat of detonation (Q), detonation velocity (D), and detonation pressure (P), were evaluated to be, for 1: 1.123 kcal·g<sup>-1</sup>, 7.971 km·s<sup>-1</sup> and 30.8 GPa; for 2: 2.165 kcal $\cdot$ g<sup>-1</sup>, 8.846 km $\cdot$ s<sup>-1</sup> and 35.3 GPa. 1 and 2 are insensitive to impact and friction. As combustion promoter, both of complexes can effectively accelerate the thermal decomposition of ammonium perchlorate (AP).

### **1. INTRODUCTION**

Energetic materials play an irreplaceable role in military, aerospace, civil and others [1-8]. In the past few decades, heterocyclic ring explosives based on conventional PETN, nitramine (RDX and HMX) [9] and nitroaromatic group (TNT and TATB) [10-12] have constantly been synthesized. High-nitrogen heterocyclic systems are one of useful and promising structures for the design and synthesis of energetic materials because of the inherently energetic N-N, N=N and C-N bonds, and high ring strain, such as azoles, azines, furazans and their derivatives [13-18].

The inherent contradiction between high energy and insensibility is a major problem in constructing energetic materials. In order to keep the balance of energy and sensibility, energetic complexes have caused close attention in recent years. As an insensitive energetic unit, furazan ring is focused on. Because large  $\pi$  bonds and approximate coplanar atoms, the structure is denser when forming crystals [19]. At known, the oxygen atom in the ring is highly active and can act as an oxidizing agent [20-24]. For these considerations above, it seems attractive enough to construct energetic complexes with furazan group as energy carrier. Unfortunately, furazacycline is of non-liable coordination group, and only a few complexes directly coordinate with N atoms in furazan [25-27]. In order to improve the activity of N atoms, an electron-rich group hydroxyl group is introduced in its ortho carbon atom.

3-nitro-4-(tetrazol-5-yl) furazan (NTZF: N = 53.60%), which was used as the starting materials for synthesis. [28] In aqueous solution, the hydroxyl group from water molecule can attack the carbon cation to replace the nitro group, producing hydroxyl-4-(tetrazol-5-yl) furazan (HTZF). Compared with NTZF, HTZF is apt to participates in coordination to form complexes with the activated ortho nitrogen atom in the one-pot reaction (Scheme 1). In the present work, we obtained cobalt(II) and zinc(II) energetic complexes with HTZF and structurally characterized. TG analysis reveals that two 3D surpramolecule complexes have good thermal stability. Detonation property reveals that **2** has better performance. Their thermodynamic parameter  $\Delta G^{\neq}$ ,  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$ , detonation properties and sensitivities were also

investigated. Moreover, the performances of the two complexes thermal decomposition of AP were explored.

#### Scheme 1

Syntheses of complexes 1 and 2.



### 2. EXRERIMENTAL SECTION

Caution: Ligands and the target complexes are hazardous materials, which explosion may occur under certain conditions. The necessary safety precautions should be used during the experiment, especially when the complexes are prepared on a large scale.

### 2.1. Materials and instruments

All starting materials are commercially available and were used without any purification. Elemental analyses were carried out with an Elementar Vario EL III analyzer. IR spectra were recorded with a Tensor 27 spectrometer (Bruker Optics, Ettlingen, Germany). TG and DSC analyses were conducted on a Netzsch STA 449C instrument using nitrogen gas as atmosphere. About 0.7 mg of samples was used for each measurement. The specific procedures are described as follows: the standard weights were used for the calibration of the balance. In the range of 30-800 °C, the baseline was calibrated with an empty crucible at a heating rate of 10 °C min<sup>-1</sup> and a flowing rate of 10 mL min<sup>-1</sup> of nitrogen gas. X-ray powder diffraction measurements were performed on a Rigaku RU200 diffractometer at 60 kV, 300 mA and Mo Kα

radiation ( $\lambda = 0.71073$  Å).

#### 2.2 Synthesis of complexes 1 and 2

#### 2.2.1. Synthesis of 3-amino-4-(tetrazol-5-yl) furazan (ATZF)

ATZF prepared procedure was using the optimized 3-Amino-4-aminohydrazolyfurazan (AFAD) (2.00 g, 12.66 mmol) and 40 mL of 2.0% hydrochloric acid were added into a three-necked round-bottomed flask fitted with a mechanical stirrer and a dropping funnel. 10% NaNO<sub>2</sub> solution (10 mL) was added dropwise at 0 °C. Upon complete addition, continuous stirring has been held for 2 hours at 15 °C. The yellow precipitate was filtered and 1.65 g yellow solid was collected with a yield of 76.7%. The product was crystallized from water with a melting point of 210-211 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz) δ: 6.59 (s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 500 MHz) δ: 155.44, 147.49, 136.20; IR (KBr) v: 3458, 3357 (NH<sub>2</sub>), 3050 (N-H), 1641, 1622 (C=N) cm<sup>-1</sup>. Anal. calcd for C<sub>3</sub>H<sub>3</sub>N<sub>7</sub>O: C 23.53, N 64.05, H 1.961; found: C 23.84, N 64.06, H 1.956.

### 2.2.2. Synthesis of 3-nitro-4-(tetrazol-5-yl) furazan (NTZF)

NTZF was prepared using the optimized procedure [28]. The mixture of Na<sub>2</sub>WO<sub>4</sub> (6.60 g, 0.011 mol) and 50% hydrogen peroxide solution (90.00 g, 1.32 mol) was placed in a three-necked round-bottomed flask with a stirrer and dropping funnel in an ice-salt bath at -10 °C. To which sulfuric acid (88.0 g) was added dropwise under stirring at 5 °C. Then, the reaction mixture was warmed up to room temperature and 3-amino-4-cyanofurazan (1.6 g, 14.55 mmol) was added slowly. After 3-amino-4-cyanofurazan was added completely, the reaction mixture was kept stirring at room temperature for another 3 hours and extracted with  $CH_2Cl_2$  (50 mL × 4). The combined extracts were washed with ice-water and dried on MgSO<sub>4</sub>. The yellow precipitate obtained was concentrated on a rotary evaporator to leave 1.5 g solid with a yield of 83.3%. The crude compound was crystallized from ethyl acetate with a melting point of 123-124 °C. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$ : 159.62, 146.96, 140.93; IR (KBr) v: 3250 (broad, N-H), 1566, 1345 (NO<sub>2</sub>), 1622 (C=N) cm<sup>-1</sup>. Anal. calcd for C<sub>3</sub>HN<sub>7</sub>O<sub>3</sub>: C 19.67, N 53.55, H 0.55; found: C 19.63, N 54.01, H 0.58

### 2.2.3. Synthesis of $\{[Zn(HTZF)(H_2O)_3] \cdot H_2O\}_n$ (1)

A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol, 0.030 g), NTZF (0.1 mmol, 0.015 g) and distilled water (5 mL) were kept stirring for 2 hours, and sealed in a 15 mL Teflon-lined stainless autoclave at 150 °C for 3 days. After slowly cooling to room temperature with a cooling rate of 5 °C min<sup>-1</sup>. The mixture was filtrated and left at room temperature with slow evaporation for several days. The colorless transparent crystals of **1** were collected by filtration (yield: 82%, based on NTZF). Elemental analysis (%) calcd for  $C_3H_8N_6O_6Zn$ : C, 12.45; H, 2.76; N, 29.02. Found: C, 12.50; H, 2.69; N, 29.08. IR (cm<sup>-1</sup>, KBr): 3212s, 3362m, 1625m, 1569s, 1470w, 1186w, 995m, 879m, 775m, 617w. PXRD patterns of **1** is given in Fig. **\$1**.

### 2.2.4. Synthesis of $\{ [Co(HTZF)(H_2O)_3] \cdot 2H_2O \}_n$ (2)

**2** was prepared according to the same synthetic procedure as that of **1**. A mixture of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol, 0.037 g), NTZF (0.1 mmol, 0.015 g) and distilled water (8 mL) was kept stirring for 2 hours, and sealed in a 15 mL Teflon-lined stainless autoclave at 120 °C for 3 days. Upon cooling to room temperature with a cooling rate of 5 °C min<sup>-1</sup>, the mixture was filtrated and left at room temperature with slow evaporation for several days. The orange block-like crystals of **2** were collected by filtration (yield: 70%, based on NTZF). Elemental analysis (%) calcd for C<sub>3</sub>H<sub>10</sub>N<sub>6</sub>O<sub>7</sub>Co: C, 11.96; H, 3.32; N, 27.91. Found: C, 12.03; H, 3.30; N, 28.01. IR (cm<sup>-1</sup>, KBr): 3349s, 1623m, 1567s, 1466w, 1396w, 1178m, 999m, 881m, 772w, 704w, 620w. PXRD patterns of **2** is given in Fig. S2.

#### 2.3. X-ray crystallography

The single-crystal X-ray diffraction data of **1** and **2** were collected using a Bruker Smart Apex CCD diffractometer equipped with a graphite monochromatized Mo K $\alpha$ radiation ( $\lambda = 0.71073$  Å) using  $\omega$  and  $\varphi$  scan modes. The single crystal structure was solved by direct methods using SHELXS-97 [29] and refined by means of full-matrix least-squares procedures on  $F^2$  and the SHELXL-97 [30] program. All non-H atoms were located using subsequent Fourier-difference methods and refined anisotropically.

Experimental details for the structural determination of the complexes are summarized in Table S1. Selected bond lengths and bond angles of **1** and **2** are listed in Tables S2 and S3, respectively. Further information on the crystal structure determination in crystallographic information framework (CIF) format is available in the ESI.

### **3. RESULTS AND DISCUSSION**

#### **3.1 Structural description**

Crystal structure of 1. X-ray structural analysis shows that crystallizes in the monoclinic space group  $P2_1/c$ . One  $Zn^{2+}$  ion, one ligand, three coordinated water molecules and one free water molecules are present in the asymmetric unit. As shown in Fig.1a, Zn1 is coordinated in a slightly distorted octahedral geometry environment in which the basal plane is formed by two nitrogen atoms and two oxygen atoms from two ligands (oxygen is derived from the hydroxyl group, which is generated by the attack of nitro-linked carbon cations from water.) (Zn1-N4=2.067 Å, Zn1-O2=2.126 Å) and two oxygen atoms from two water molecules (Zn1-O3 = 2.191 Å) in the axial position. The ligands coordinate to Zn1 with bidentate chelating coordination modes (Fig. 1a). Zn2 is also coordinated in octahedral geometry environment in which the basal plane is formed by four oxygen atoms from two water molecules (Zn2-O4 =2.103 Å, Zn2-O5 = 2.135Å) and two nitrogen atoms from two ligands (Zn2-N6 = 2.114 Å) in the axial position, and the ligands coordinate to Zn2 with bridging coordination mode. Each ligand links two Zn<sup>2+</sup> ions to generate a 1D infinite chain. The interaction of the coordination waters through hydrogen bonds makes the 1D chains form a 3D supramolecular structure. Lattice waters are also involved in the formation of hydrogen bonds, making 3D structure more compact. (N-H...O, O-H···O, O-H···N). The detailed hydrogen bond interaction information is shown in Table S4.

**Crystal structure of 2.** X-ray structural analysis reveals that crystallizes in the monoclinic space group  $P2_1/c$ . The asymmetric unit of **2** contains one Co<sup>2+</sup> ion, two

ligands, three coordinated water molecules and two free water. As shown in Fig. 2a,  $Co^{2+}$  is coordinated in a slightly distorted octahedral geometry environment in which the basal plane is formed by four oxygen atoms from one ligand (Oxygen is derived from the hydroxyl group, which is generated by the attack of nitro-linked carbon cations from water.) and three coordinated water molecules (Co-O2 = 2.055 Å, Co-O3 = 2.090 Å, Co-O4 = 2.089 Å, Co-O5 = 2.074 Å), respectively. The axial position is defined by two nitrogen atoms (Co-N1 = 2.112 Å, Co-N6 = 2.172 Å) which belongs to two ligands. Each ligand links two Co(II) ions to form a 1D infinite chain, where the ligands coordinate to Co(II) with bidentate chelating coordination and bridging coordination modes. The 1D infinite chains are further fabricated into a 3D supramolecular structure just through  $\pi \cdots \pi$  stacking and coordination waters. Like 1, lattice waters play a significant role in stabilizing structure (Fig. 2c-2d).



**Fig. 1.** (a) The coordination environment of the  $Zn^{2+}$  ion and ligand HTZF, (b) The 1D chain in **1**, and (c) 3D supramolecular structure of **1**, where the green dashed lines represent hydrogen bonds.

#### **3.2.** Thermal stability

The themodecomposition reactions of crystalline samples of **1** and **2** were measured with a linear heating rate of 10  $^{\circ}$ C min<sup>-1</sup> in nitrogen atmosphere. As shown in Fig. 3a, there are one endothermic peak and one exothermic peak for **1**. The range of endothermic progress starts from 76  $^{\circ}$ C to 140  $^{\circ}$ C with the peak temperature of 106  $^{\circ}$ C, which confirms that loss part of water molecules. The exothermic peak temperature of 293.0  $^{\circ}$ C shows the partial collapse of the framework. It isn't completely collapsed until 800  $^{\circ}$ C. For **2**, there are two peaks in DSC curve. One is an endothermic peak with a peak temperature of 148.7  $^{\circ}$ C, which is ascribed to a dehydration process. The exothermic peak is the main decomposition process with the peak temperature of 295.8  $^{\circ}$ C.



**Fig. 2.** (a) The coordination environment of the Co<sup>2+</sup> ion and ligand HTZF, (b) The 1D chain structure of **2**, and (c) The 3D supramolecular structure of **2**. (d) Adjacent tetrazolyl and furazan rings showing the  $\pi \cdots \pi$  stacking interactions.

For both **1** and **2**, decomposition temperatures are above 290 °C, revealing their good thermal stabilities, which is presumably attributed to extensive intermolecular interactions. As noticed, TG curve is more gently and DSC curve emits less heat for **1**, which is ascribed to the existence of hydrogen bonds in **1**. To our surprise, **2** (2 mg)<sup>4</sup> was heated in nitrogen atmosphere at temperature above 150 °C, there was a violent explosion, which indicates that lattice water plays an important role in reducing complexes sensitivity.

#### 3.3. Non-isothermal kinetics analysis

The thermokinetic parameters of decomposition processes of **1** and **2** were discussed by Kissinger's method [31] and Ozawa's method [32,33]. The equations can be used to estimate the rate constants of the thermal decomposition processes of **1** or **2**. The Kissinger (1) and Ozawa (2) equations are as follows, respectively:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E}{RT_p}$$
(1)  
$$\log \beta + \frac{0.4567E}{RT_p} = C$$
(2)

where *E* is the apparent activation energy; *A* is the pre-exponential factor;  $T_p$  is the peak temperature; *R* is the gas constant, 8.314 J mol<sup>-1</sup> K<sup>-1</sup>;  $\beta$  is the linear heating rate and *C* is a constant. The exothermic peak temperature was measured from DSC curves at heating rates of 2, 5, 8 and 10 °C min<sup>-1</sup>. The apparent activation energies  $E_k$ and  $E_0$ , pre-exponential factor  $A_k$  and linear correlation coefficients  $R_k$  and  $R_0$  were determined and are shown in Table 1. The calculate results are similar with both methods and within the normal range of deviation allowed. The Arrhenius equations can be expressed by using  $E_a$  (the average of  $E_k$  and  $E_0$ ) and lnA values, as follows: ln  $k = 23.57 - 272.05 \times 10^3/RT$  for 1, and ln  $k = 23.52 - 272.88 \times 10^3/RT$  for 2. Additionally, the entropies of activation ( $\Delta S^{\neq}$ ), enthalpies of activation ( $\Delta H^{\neq}$ ), and free energies of activation ( $\Delta G^{\neq}$ ) of 1 and 2 were calculated and listed in Table 2. The thermokinetic analysis shows that the initial thermal decomposition reactions are of non-spontaneous enthalpy-driven process.



Fig. 3. (a) DSC curves of 1 and 2, and (b) TG curves of 1 and 2.

Table 1	
Thermokinetic parameters of decomposition reaction	s for 1 and 2.

Complex	1	2
Heating rates (°C min <sup>-1</sup> )	Peak temperature (°C)	Peak temperature (°C)
2	278.0	278.0
5	285.9	286.0
8	290.0	290.1
10	293.0	295.8
Kissinger's method		
$E_{\rm k}$ (kJ mol <sup>-1</sup> )	274.36	275.19
$\ln A_k$ (s <sup>-1</sup> )	23.5692	23.5170
$R_{\rm k}$	0.9980	0.9982
Ozawa–Doyle's method		
$E_{\rm o}$ (kJ mol <sup>-1</sup> )	269.73	270.56
R <sub>o</sub>	0.9981	0.9983

### Table 2

Thermodynamic parameters of decomposition reactions for 1 and 2.

Complex	$\Delta G^{\neq} (\mathrm{KJ} \cdot \mathrm{mol}^{-1})$	$\Delta H^{\neq} (\mathrm{KJ} \cdot \mathrm{mol}^{-1})$	$\Delta S^{\neq} (\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})$
1	302.79	267.34	-62.62
2	304.06	268.15	-63.12

#### 3.4. Heat of detonation

The heat of detonation (*Q*), detonation velocity (*D*) and detonation pressure (*P*) are significant parameters for energetic materials. We obtained *Q*, *D* and *P* of complexes by density functional theory (DFT) and Kamlet-Jacobs equations. The energy of detonation ( $\Delta E_{det}$ ) was computed by the equation:  $\Delta E_{det} = -[\Delta_f H_m^{\theta}(\text{detonation products}) - \Delta_f H_m^{\theta}(\text{explosive})]$ . Using a linear correlation ( $\Delta H_{det} = 1.127\Delta E_{det} + 0.046$ , r = 0.968) to estimate the heat of detonation ( $\Delta H_{det}$ ), which is widely used in the evaluation of the heat of detonation of explosives [34,35]. For both 1 and 2, water, carbon dioxide, nitrogen and carbon were considered to be the decomposition products of the organic components and all the nonmetallic products are treated as gas. The detonation reactions are described using the following equations:

$$ZnC_3N_6O_6H_8 \rightarrow ZnO + 4H_2O + 1/2CO_2 + 3N_2 + 5/2C$$
 (3)

$$CoC_3N_6O_7H_{10} \rightarrow CoO + 5H_2O + 1/2CO_2 + 3N_2 + 5/2C$$
 (4)

The DFT calculate values for 1 and 2 are listed in Table S5.

#### 3.5. Characterization of the detonation velocity and detonation pressure

The characteristics of energetic materials is evaluated by its detonation velocity (D) and detonation pressure (P), and they can be estimated based on Kamlet-Jacobs equations [35].

$$D = 1.01\Phi^{1/2}(1+1.30\rho)$$
$$P = 1.558\Phi\rho^{2}$$
$$\Phi = 31.68N(MQ)^{1/2}$$

where *D* is the detonation velocity (km s<sup>-1</sup>) and *P* is the detonation pressure (GPa),  $\rho$  is the density of the explosive (g cm<sup>-3</sup>), *N* is the number of moles of detonation gases per gram of explosive, *M* is the average molecular weight of these gases and *Q* is the heat of detonation (kcal g<sup>-1</sup>). The detonation velocity and detonation pressure of **1** and **2** are shown in the Table 3.

(5)

#### 3.6. Sensitivity tests

Sensitivity is the ability of an explosive substance to undergo an explosive change under the influence of external energy. For safety testing, the impact and friction sensitivities of **1** and **2** were measured by a Fall Hammer apparatus. Twenty milligrams of sample **1** or **2** into a copper cap, and a 2 kg weight was dropped from a set height in a 39.2 MPa press. The collected data are summarized in Table 3. The results show that the impact sensitivity of **1** and **2** are 40 J and friction sensitivity of **1** and **2** was observed at up to 36 kg (360 N).

#### 3.7. Discussion

The physical properties of **1** and **2** compared with the properties of furozan complexes and traditional energetic materials are summarized in Table 3. For **1** and **2**, heat of formation and explosive parameters are obtained by theoretical calculations. *Q*, *D* and *P* are calculated by the DFT (density functional theory) and Kamlet-Jacobs equation (**1**: 1.123 kcal·g<sup>-1</sup>, 7.971 km·s<sup>-1</sup> and 30.8 GPa; **2**: 2.165 kcal·g<sup>-1</sup>, 8.846 km·s<sup>-1</sup> and 35.3 GPa). Compared with furazan compounds, **3** and **4** show the pretty good detonation performance, but its impact and friction sensitivity are unacceptable. The detonation performance and stability of **2** are better than **5**. Compared with the complexes with triazole and tetrazole as energy units, furazan complexes perform better in detonation performance. Obviously, the impact and friction sensitivities of the complexes show excellent results. The detonation performance of **2** is superior to RDX, and the safety is higher than TNT. And its decomposition temperature reaches 295.8 °C. Obviously, **2** presents a good balance between energy and sensitivity.

Table	3
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The physicochemical properties of 1, 2 and some energetic materials.

F									
Complex	$ ho^a$	$N^{b}$	$arOmega^c$	$T_{\rm d}^{\ d}$	$Q^e$	$D^{f}$	$P^g$	$IS^h$	$FS^i$
	(g cm <sup>-3</sup> )	(%)	(%)	(°C)	(kcal g <sup>-1</sup> )	(km s <sup>-1</sup> )	(GPa)	(J)	(N)
1	2.11	29.02	-19.11	293.0	1.123	7.971	30.8	>40	>360
2	1.85	27.91	-17.27	295.8	2.165	8.846	35.3	>40	>360
3,4-Bis(4'-aminofuroxan	1.79	39.44	-11.30	183.6	_	8.480	31.0	13.0	240
o-3')furoxan(3) [36]									

3,4-Bis(4'-nitrofuroxano-	1.91	32.56	+18.60	146.5	_	9.503	40.8	3.0	40	
3')furoxan(4) [36]										
LLM-191(5) [37]	1.89	37.81	-27.00	283	1.48	8.85	36.0	—	148	
$[Co(HATT)_2(H_2O)_2]$	2.02	_	_	176	_	_	—	>40	>360	
$(ClO_4)_3 \cdot 4H_2O(6)$ [38]										
$[\text{Co}(\text{AZT})_2(\text{H}_2\text{O})_4](\text{PA})_2$	_	31.32	_	208	_	—	_	_	35.9	
(7) [39]									3	
Co(TO) <sub>2</sub> (DNBA)2(H <sub>2</sub> O)	1.684	20.38	_	238	1.726	7.834	26.13	35.3	>360	
<sub>2</sub> ( <b>8</b> ) [40]							3			
${[Cu(tztr)] \cdot H_2O}_n(9)$	2 216	45.23	_	325	1.322	7.92	31.99	>40	>360	
[41]	2.316									
$[Cd(HTRTR)_2(H_2^2O)_4]$	1.94	_	_	195.9	0.247	_		>40	>360	
(HTNR) <sub>2</sub> (10) [42]					0.247					
$[PbCu(bta)2(H_2O)_5] \cdot 2H_2$	2 415	36.07	_	231	1 507	8.751	39.61	>40	>360	
O(11) [43]	2.415				1.507					
$[Na(H_2BTT)(H_2O)_2]_n$	1 706	58.5	_	336	0.99	8.120	22.83	>40	>360	
<sub>Ta</sub> ( <b>12</b> ) [44]	1.706									
TNT [34]	1.65	18.50	-24.67	295	1.0	7.303	21.3	15.0	353	
HMX [34]	1.91	37.84	-21.61	275	_	8.900	38.4	7.0	112	
RDX [34]	1.80	37.84	-21.61	205	—	8.795	34.9	7.5	120	

<sup>*a*</sup> Density from X-ray diffraction analysis. <sup>*b*</sup> Nitrogen content. <sup>*c*</sup> Oxygen balance { $\Omega_{CO} = nO - xC - yH/2(1600/FW)$ }. <sup>*d*</sup> Temperature of decomposition by DSC. <sup>*e*</sup> Heat of detonation. <sup>*f*</sup> Detonation velocity. <sup>*g*</sup> Detonation pressure. <sup>*h*</sup> Impact sensitivity. <sup>*I*</sup> Friction sensitivity. Abbreviations: HATT = 5-(4-Amino-1,2,4-triazol-3-on-5-yl) tetrazole; AZT = 3-azido-1,2,4-triazole; TO = 1,2,4-triazole-5-one; HDNBA = 3,5-dinitrobenzoic acid; H<sub>2</sub>tztr = 3-(1H-tetrazol-5-yl)-1H-triazole; HTRTR = 4-[3-(1,2,4-triazol-yl)-1,2,4-triazole; HTNR<sup>-</sup> = styphnic acid anion; H<sub>2</sub>bta = N,N-bis(1H-tetrazole-5-yl)-amine; H<sub>3</sub>BTT = 4,5-bis(tetrazol-5-yl)-2H-1,2,3-triazole.

#### 3.7. Catalytic Effect on the Decomposition of Ammonium Perchlorate

AP is the most widely-used component of high-energy oxidant in solid propellants. The combustion process of the composite solid propellant is strongly dependent on the thermal decomposition behavior of AP. In general, the catalytic performances of burning rate catalysts in the solid propellant are often evaluated by their effects on the thermal decomposition of AP by DSC techniques. The DSC curve for thermal decomposition of AP shows one endothermic peak and two exothermic peaks. The endothermic peak at 242 °C corresponds to the morphological transition from an orthorhombic to a cubic phase of AP. The first exothermic peak at 337 °C corresponds to the low-temperature decomposition (LTD). The second exothermic

peak at 442 °C corresponds to the high-temperature decomposition (HTD). In the experiment, that mass ratio of **1** and **2** to AP is 1:3. In Fig. 4, there exhibit no effect on the morphological transition peaks for **1** and **2**. **1** has two peaks with LDT peak and HDT peak, they shift downwards about 11.2 °C and 92.3 °C, respectively. **2** combines two exothermic peaks into one intense exothermic peak at 323.5 °C. The LDT peak decreases about 13.5 °C compared with pure AP and HDT peak decreases about 118.5 °C. In summary, both **1** and **2** show good performance for the thermodecomposition of AP. Although the carbon content of **1** (12.45%) is slightly higher than **2** (12.03%), the heat release and peak temperature of **2** are better than **1**. It is possible that different metal centers will have different effects on combustion modifier. In this work, the catalytic effect of cobalt is better than that of zinc. In order to further confirm this conclusion, some published compounds of Co and Zn used as AP combustion catalysts are summarized in Table S6. As can be seen from the data, the catalytic effects of Co-centered compounds are significantly better than that of Zn.



Fig. 4. DSC curves of AP, 1+AP and 2+AP.

### 4. Conclusions

In conclusion, two furazan energetic complexes,  $\{[Zn(HTZF)(H_2O)_3] \cdot H_2O\}_n$  (1) and  $\{[Co(HTZF)(H_2O)_3] \cdot 2H_2O\}_n$  (2) were synthesized and structurally characterized. Both complexes feature excellent thermostability and insensitivity ( $T_{d,1} = 293$  °C,  $T_{d,2}$ 

= 295.8 °C). The non-isothermal kinetics analysis of the complexes indicates that the thermal decomposition process is inert and thermodynamic data reveals that is a non-spontaneous enthalpy-driven process. For 2, the detonation performance (2.165 kcal $\cdot$ g<sup>-1</sup>, 8.846 km $\cdot$ s<sup>-1</sup> and 35.3 GPa) is superior to RDX and the safety (IS>40 J, FS>360 N) is higher than TNT. As combustion rate modifier, the energetic complexes of cobalt with furazan demonstrate the promising development prospect. 2 would be potentially applied for energetic materials. JUSC

### **Conflicts of interest**

There are no conflicts to declare.

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Two energetic complexes were synthesized based on the furazan derivative, 3-hydroxyl-4-(tetrazol-5-yl) furazan (HTZF). They show well-balance between sensitivity and detonation performance. The detonation performance of **2** is superior to RDX, and the safety is higher than TNT.