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Synthesis, Crystal Structure and Thermal Behavior of $[Zn(en)_3](FOX\text{-}7)_2$

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Abstract: A new energetic Zn-FOX-7 complex $[Zn(en)_3](FOX\text{-}7)_2$ was firstly synthesized and characterized by X-ray diffraction (FOX-7, 1,1-diamino-2,2-dinitroethylene). The crystal is monoclinic, space group *C*2/c with crystal parameters of $a=0.77170(16)$ nm, $b=1.6720(3)$ nm, $c=1.6996(3)$ nm, $\beta=94.333(3)°$, $V=2.1867(7)$ nm^3, $Z=4$, $\mu=1.194$ mm^{-1}, $F(000)=1112$, $D_c=1.628$ g·cm^{-3}, $R_1=0.0359$, $wR_2=0.0955$. Thermal decomposition of $[Zn(en)_3](FOX\text{-}7)_2$ was studied by differential scanning calorimetry and thermogravimetry methods. Results show that central Zn^{2+} ion is coordinated by six N atoms from three ethylenediamine molecules, which form a distorted octahedral structure, and while $FOX\text{-}7^-$ anion has no coordination with central Zn^{2+} ion. The self-accelerating decomposition temperature and critical temperature of thermal explosion of $[Zn(en)_3](FOX\text{-}7)_2$ are 167.1 ℃ and 168.8 ℃, respectively. $[Zn(en)_3](FOX\text{-}7)_2$ exhibits lower thermal stability than $Zn(NH_3)_2(FOX\text{-}7)_2$. The impact sensitivity of $[Zn(en)_3](FOX\text{-}7)_2$ is about 20.6 J.

Key words: structural chemistry; 1,1-diamino-2,2-dinitroethylene(FOX-7); zinc complex; crystal structure; thermal behavior

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1 Introduction

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high-energy material with high thermal stability and low sensitivity to impact and friction. It has a density of 1.885 g·cm^{-3}, a heat of formation of 133.7 kJ·mol^{-1}, a same insensitivity to TATB (1,3,5-triamino-2,4,6-trinitrobenzene) and a similar energy density with RDX (1,3,5-trinitroperhydro-1,3,5-triazine) and HMX (cyclotetramethylene tetranitramine) [1]. Since firstly synthesized in 1998[1], FOX-7 has received much attentions as the main component used in insensitive ammunitions and solid propellants. Many researches have been carried out on the synthesis, mechanism, molecule structure, thermal behavior, explosion performance and application of FOX-7 [1-21]. FOX-7 is a representative "push-pull" nitro-enamine compound, which possesses a highly polarized carbon-carbon double bond with positive and negative charges stabilized by the amino group and nitro group respectively, and presents certain acidic properties [10, 22]. So, FOX-7 can react with strong alkalis to prepare some energetic salts, such as potassium salt, rubidium salt, cesium salt and guanidine salt [23-26]. Other salts and metal complexes of FOX-7 also can be synthesized through replacement reaction. Garg S[27-28] and He F[30] et al reported Ag(amine)(FOX-7) [amine: ammonia, methylamine and propylamine], Cu(amine)$_2$(FOX-7)$_2$ [amine: ammonia, methylamine, propylamine and dimethylamine, ethylenediamine and 1,3-propane diamine] and other copper (nickel) bipyridyl (phenanthroline) FOX-7 complexes. In this paper, new zinc-FOX-7 complex was firstly synthsized, and its crystal structure and thermal behavior were studied by X-ray diffraction, differential scanning calorimetry and thermogravimetry methods.

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2 Experimental

2.1 Synthesis of the title complex

K(FOX-7)·H_2O (0.01 mol, 1.88 g) was put into excess 67% ethylenediamine (15 mL) to clear solution, and then $Zn(NO_3)_2\cdot 6H_2O$ (0.005 mol, 1.49 g) was added to it. After reaction at room temperature for 20 min, the resulting mixture was stored at room temperature for some time. Then many yellow crystals of $[Zn(en)_3](FOX\text{-}7)_2$ were formed, which were filtered, washed with water and dried under vacuum. IR (KBr, ν/cm^{-1}): 3414, 3332, 3294, 2943, 2883, 1641, 1493, 1354, 1247, 1132, 1012, 828, 750, 629, 504. Elemental anal: calcd. (%) for $C_{10}H_{30}N_{14}O_8Zn$: C 22.25, H 5.60, N 36.32; found: C 22.19, H 5.71, N 36.25.

2.2 Determination of the single crystal structure

A light yellow crystal with dimensions of 0.35 mm×0.21 mm×0.19 mm was chosen for X-ray determination. The data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073Å). The structure were solved by the direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms[31-32]. The hydrogen atoms were added according to the theoretical molecular models. Crystal data and refinement results are summarized in Table 1 (CCDC No.: 946932.).

2.3 Thermal decomposition

The differential scanning calorimetry (DSC) was performed using a DSC 200F3 apparatus (NETZSCH, Germany) under a nitrogen atmosphere at a flow rate of 80 mL·min^{-1}. The sample

mass used in experiment was about 0.6 mg. The heating rates were 5.0, 7.5, 10.0, 12.5, 15 ℃ · min^{-1}, respectively, and temperature range was from room temperature to 450 ℃.

Table 1 Crystal data and structure refinement details for [Zn(en)$_3$](FOX-7)$_2$

chemical formula	$C_{10}H_{30}N_{14}O_8Zn$
formula weight	539.84
temperature/K	296(2)
crystal system	monoclinic
space group	*C*2/*c*
a/nm	0.77170(16)
b/nm	1.6720(3)
c/nm	1.6996(3)
β / (°)	94.333(3)
volume/nm^3	2.1867(7)
Z	4
D_c/g · cm^{-3}	1.628
absorption coefficient/mm^{-1}	1.194
F(000)	1112
θ/ (°)	2.44 ~ 25.07
index ranges	$-9 \leqslant h \leqslant 7$ $-19 \leqslant k \leqslant 19$ $-20 \leqslant l \leqslant 20$
reflections collected	5363
reflections unique	1935 [R(int) = 0.0219]
completeness to theta = 25.07%	99.9
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	1.064
final R indices [$I>2\sigma(I)$]	R_1 = 0.0359 wR_2 = 0.0955
R indices (all data)	R_1 = 0.0391 wR_2 = 0.0978
largest diff. peak and hole /e · Å^{-3}	0.415 and −0.335

The thermogravimetry was performed using a SDT-Q600 apparatus (TA, USA) under nitrogen at a flow rate of 100.0 mL · min^{-1}. The sample mass was 0.76 mg and heating rate was 10.0 ℃ · min^{-1}. Temperature range was from room temperature to 450 ℃.

The impact sensitivity was determined based on GB/T21567–2008 by using a ZBL-B impact sensitivity instrument (Nachen Co., China). The mass of drop wight is 2.0 kg. The sample mass for each test is 30 mg.

3 Results and discussion

3.1 Crystal structure

Crystal structure and crystal packing of [Zn(en)$_3$](FOX-7)$_2$ are illustrated in Fig.1 and Fig.2. Selected bond lengths and bond angles of [Zn(en)$_3$](FOX-7)$_2$ are summarized in Table 2.

[Zn(en)$_3$](FOX-7)$_2$ crystallizes in the monoclinic crystal system with space group C2/c containing four molecules per unit cell. As shown in Fig.1, [Zn(en)$_3$](FOX-7)$_2$ is formed of one $[Zn(en)]_3^{2+}$ ion and two FOX-7$^-$ anions. The whole complex exhibits a centrosymmetric structure around Zn^{2+} ion (symmetry transformation: -x, y, -z+1/2). Central Zn^{2+} ion is coordinated by six N atoms from three ethylenediamine molecules, and two FOX-7$^-$ anions symmetrically distribute in both sides of $[Zn(en)]_3^{2+}$ ion and have no coordination with central Zn^{2+} ion. Six N atoms around central Zn^{2+} ion form a distorted octahedral structure. At first, we predict the complex should be Zn(en)(FOX-7)$_2$ including one ethylenediamine molecule or Zn(en)$_2$(FOX-7)$_2$ including two ethylenediamine molecules, and two FOX-7$^-$ anion should be involved in coordination, but the result is unexpected. It is different from that of analogous Zn(NH$_3$)$_2$(FOX-7)$_2$, which is a four-coordination structure, two FOX-7$^-$ anions all have coordination with central Zn^{2+} ion [33]. According to the structure of analogous Cu(en)$_2$(FOX-7)$_2$(H$_2$O)$_2$[28], the coordination structure of [Zn(en)$_3$](FOX-7)$_2$ is reasonable. In addition, there are six kinds of N—H ··· O hydrogen-bond interactions and one kind of N—H ··· N hydrogen-bond interaction in [Zn(en)$_3$](FOX-7)$_2$. It is the coordination interactions, electrostatic attractions and hydrogen-bond interactions that form the order crystal packing of [Zn(en)$_3$](FOX-7)$_2$(Fig. 2).

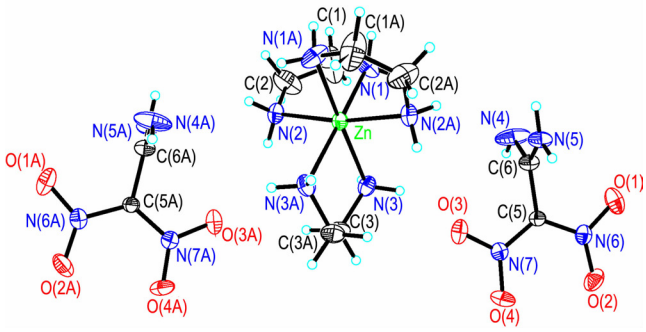


Fig. 1 Crystal structure of [Zn(en)$_3$](FOX-7)$_2$ with 30% probability level

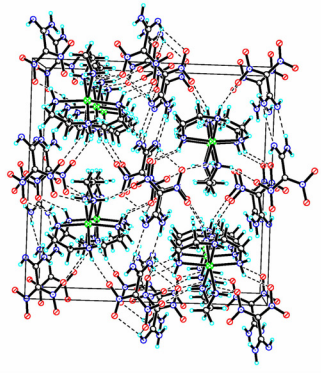


Fig. 2 Packing of molecular [Zn(en)$_3$](FOX-7)$_2$ in crystal lattice

To $[Zn(en)_3]^{2+}$, three ethylenediamine molecules exhibit different configurations because of different positions and hydrogen-bond interactions, supporting by the bond lengths [Zn(1)—N(1)(0.2228 nm), Zn(1)—N(2) (0.2177 nm) and Zn(1)—N(3) (0.2201 nm)] and bond angles [N(2)—Zn(1)—N(2)A (170.49°), N(2)—Zn(1)—N(3) (91.89°) N(2)A—Zn(1)—N(3) (95.36°), N(3)—Zn(1)—N(3)A (80.51°), N(2)—Zn(1)—N(1)A (94.25°), N(3)—Zn(1)—N(1)A (172.44°), N(2)—Zn(1)—N(1) (79.03°), N(3)—Zn(1)—N(1) (94.51°), N(1)A—Zn(1)—N(1) (90.99°)]. The self-symmetry ethylenediamine molecule presents greater distortion than other two symmetric ethylenediamine molecules, according to the bond lengths of C(1)—C(2) (0.1361 nm) and C(3)—C(3)A(0.1509 nm), bond angles of

N(2)—Zn(1)—N(1)(79.03°) and N(3)—Zn(1)—N(3)A (80.51°), and torsion angles of N(3)—C(3)—C(3)A—N(3)A (−57.8°) and N(2)—C(2)—C(1)—N(1)(14.1°).

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

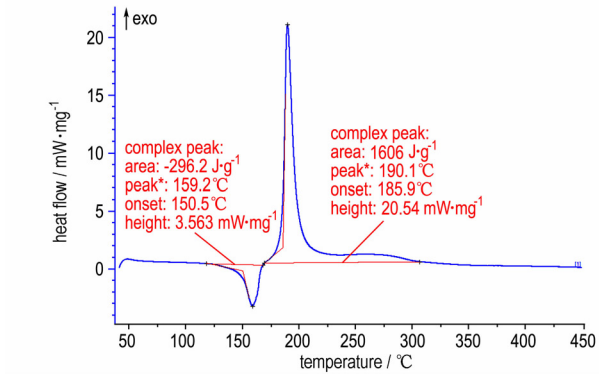
bond	length/nm	bond	angle/(°)
Zn(1)—N(1)	0.2228(3)	N(2)—Zn(1)—N(2)A#1	170.49(14)
C(6)—N(5)	0.1333(4)	C(2)—N(2)—Zn(1)	111.3(2)
Zn(1)—N(2)	0.2177(2)	N(2)—Zn(1)—N(3)	91.89(10)
C(6)—C(5)	0.1498(4)	C(3)—N(3)—Zn(1)	107.30(18)
Zn(1)—N(3)	0.2201(2)	N(2)A#1—Zn(1)—N(3)	95.36(9)
N(7)—C(5)	0.1374(3)	N(4)—C(6)—N(5)	121.4(3)
N(1)—C(1)	0.1425(5)	N(3)—Zn(1)—N(3)A#1	80.51(13)
C(1)—C(2)	0.1361(6)	N(4)—C(6)—C(5)	120.4(3)
N(2)—C(2)	0.1430(5)	N(2)—Zn(1)—N(1)A#1	94.25(10)
C(3)—C(3)A#1	0.1509(6)	N(5)—C(6)—C(5)	118.2(2)
N(3)—C(3)	0.1476(4)	N(3)—Zn(1)—N(1)A#1	172.44(9)
N(6)—C(5)	0.1382(3)	C(2)—C(1)—N(1)	121.4(3)
C(6)—N(4)	0.1299(4)	N(2)—Zn(1)—N(1)	79.03(10)
C(1)—C(2)	0.1361(6)	C(1)—C(2)—N(2)	118.5(3)
		N(2)A—Zn(1)—N(1)	94.25(10)
		N(3)—C(3)—C(3)A#1	109.8(2)
		N(3)—Zn(1)—N(1)	94.51(12)
		N(7)—C(5)—N(6)	122.7(2)
		N(3)A—Zn(1)—N(1)	172.44(9)
		N(7)—C(5)—C(6)	118.8(2)
		N(1)A—Zn(1)—N(1)	90.99(18)
		N(6)—C(5)—C(6)	118.5(2)
		C(1)—N(1)—Zn(1)	107.9(2)

symmetry transformation: #1 −x, y, −z+1/2

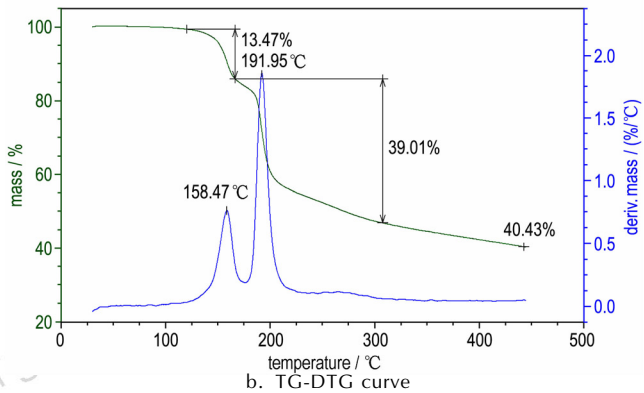
The space configuration of $FOX\text{-}7^-$ anion changes from one plane to two approximate orthogonal planes (no-hydrogen atoms)[2], according to the torsion angles of N(4)—C(6)—C(5)—N(7) (−96.0°), N(5)—C(6)—C(5)—N(7) (84.9°), N(4)—C(6)—C(5)—N(6) (−87.3°) and N(5)—C(6)—C(5)—N(6) (−91.9°), and the intersection of the two approximate orthogonal planes is C(5)—C(6) bond, which can also be found in other salts of FOX-7[23-24]. The bond lengths and bond angles change greatly from molecular state to ionic state. The oretical C(5)—C(6) double bond (0.1498 nm) in $FOX\text{-}7^-$ anion is much closer to C—C single bond (0.153 nm) than that in FOX-7 molecule. Equilong C(6)—N(4) and C(6)—N(5) bonds present big deviation (0.1299 and 0.1333 nm). C(6)—N(4) in $FOX\text{-}7^-$ anion is a typical C—N double bond. FOX-7 has changed into its one tautomer format.

3.2 Thermal behavior

Typical DSC and TG-DTG curves in Fig.3 indicate that the thermal decomposition behavior of $[Zn(en)_3](FOX\text{-}7)_2$ can be divided into two obvious stages. The first stage is an endothermic melting-decomposition process, which occurs at 120 ~ 165 ℃ with a mass loss of about 13.5%, which is consistent with the theoretical value (11.2%) of losing one ethylenediamine molecule. The extrapolated onset temperature, peak temperature and decomposition enthalpy of the process are 150.5, 159.2 ℃ and 296.2 J·g^{-1} at a heating rate of 10.0 ℃·min^{-1}, respectively. The second stage is an intense exothermic decomposition process with a mass loss of about 32.1% at 165 ~310 ℃, and the extrapolated onset temperature, peak temperature and decomposition enthalpy of the process are185.9 ℃, 190.1 ℃ and −1606 J·g^{-1} at a heating rate of 10.0 ℃·min^{-1}, respectively. The final residue at 450 ℃ is about 40.4%, which should contain ZnO (15.2%) and some organic matters. The thermal behavior of $[Zn(en)_3](FOX\text{-}7)_2$ is much different from that of $Zn(NH_3)_2(FOX\text{-}7)_2$, which exhibits two continuous exothermic decomposition processes without melting process, and the extrapolated onset temperature and peak temperature of the first decomposition are 198.1 ℃ and 204.4 ℃, respectively, at a heating rate of 10.0 ℃·min^{-1}[33]. It shows the thermal stability of $Zn(NH_3)_2(FOX\text{-}7)_2$ is better than that of $[Zn(en)_2](FOX\text{-}7)_2$.



a. DSC curve



b. TG-DTG curve

Fig. 3 DSC (a) and TG/DTG (b) curves of $[Zn(en)_3](FOX\text{-}7)_2$ at a heating rate of 10.0 ℃·min^{-1}

A multiple heating method was employed to obtain the kinetic parameters (apparent activation energy (E) and pre-exponential constant (A)) of the exothermic decomposition (Table 3). The calculated results in table 3 indicate that the apparent activation energy obtained by Kissinger method (E_k) is consistent with that by Ozawa method (E_o)[34-35]. The linear correlation coefficients (r_k and r_o) are all close to 1. Moreover, the apparent activation energy of the exothermic decomposition process is low, indicating that $[Zn(en)_3](FOX\text{-}7)_2$ is easy to exothermically decompose at temperature above 165 ℃.

3.3 Self-accelerating decomposition temperature and critical temperature of thermal explosion

The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are two im-

portant parameters for energetic materials, which are required to ensure safe storage and process operations and then to evaluate the thermal stability. T_{SADT} and T_b can be obtained by Eq. (1) and Eq. (2)[36-37], respectively.

Table 3 T_e, T_p and kinetic parameters of $[Zn(en)_3](FOX\text{-}7)_2$ at various heating rates

β /K·min^{-1}	T_e /℃	T_p /℃	E_k /kJ·mol^{-1}	lg (A/s^{-1})	r_k	E_o /kJ·mol^{-1}	r_o
5.0	177.4	181.5					
7.5	183.2	185.8					
10.0	185.9	190.1	137.7	13.65	0.9982	138.2	0.9984
12.5	189.4	192.3					
15.0	192.9	194.7					

Note: T_e, extrapolated onset temperature; T_p, peak temperature; β, the heating rate; Subscript k, data obtained by Kissinger method; subscript o, data obtained by Ozawa method.

$$T_{SADT} = T_{e0} = T_{ei} - n\beta_i - m\beta_i^2 \qquad i = 1-5 \tag{1}$$

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O RT_{e0}}}{2R} \tag{2}$$

where R is the gas constant; T_{e0} is the value of T_e corresponding to $\beta \to 0$; n and m are coefficients.

T_{SADT} and T_b for $[Zn(en)_3](FOX\text{-}7)_2$ are 167.1 ℃ and 168.8 ℃, respectively, which are much lower than those of $Zn(NH_3)_2(FOX\text{-}7)_2$ (183.2 ℃ and 195.8 ℃)[33].

3.4 Sensitivity

The experimental results indicate that the characteristic drop-height of impact sensitivity (H_{50}) of $[Zn(en)_3](FOX\text{-}7)_2$ is 105 cm (about 20.6 J), which is much lower than that of $Zn(NH_3)_2(FOX\text{-}7)_2$ (9 J) and RDX(7.4 J)[33,38].

4 Conclusions

(1) $[Zn(en)_3](FOX\text{-}7)_2$ was first synthesized and structurally determined by single crystal X-ray diffraction. The crystal of $[Zn(en)_3](FOX\text{-}7)_2$ is the monoclinic crystal system with space group $C2/c$. Central Zn^{2+} ion is coordinated by six N atoms from three ethylenediamine molecules to form a distorted octahedral structure, and while $FOX\text{-}7^-$ anion has no coordination with central Zn^{2+} ion.

(2) The thermal decomposition of $[[Zn(en)_3](FOX\text{-}7)_2$ exhibits two processes. The apparent activation energy and pre-exponential constant of the exothermic decomposition process are 137.7 kJ·mol^{-1}, and $10^{13.65}$ s^{-1}, respectively. $[Zn(en)_3](FOX\text{-}7)_2$ is easy to exothermically decompose at temperature above 165 ℃, and relatively less sensitive.

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$[Zn(en)_3](FOX\text{-}7)_2$ 的合成、晶体结构和热行为

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摘 要： 合成了一种新型含能锌配合物 $[Zn(en)_3](FOX\text{-}7)_2$，并测定其晶体结构。该晶体属单斜晶系，空间群 *C*2/c，晶胞参数为：*a*=0.77170(16) nm，*b*=1.6720(3) nm，*c*=1.6996(3) nm，β=94.333(3)°，*V*=2.1867(7) nm^3，*Z*=4，μ=1.194 mm^{-1}，*F*(000)=1112，D_c=1.628 g·cm^{-3}，R_1=0.0359，wR_2=0.0955。中心锌离子与三个乙二胺分子中的六个 N 原子发生配位，形成了一个畸变的八面体结构，$FOX\text{-}7^-$阴离子并未与中心 Zn^{2+}发生配位作用，而以外界离子的形式存在于分子结构中。用非等温 DSC，TG/DTG 法研究了 $[Zn(en)_3](FOX\text{-}7)_2$ 的热分解行为，其自加速分解温度和热爆炸临界温度分别为 167.1 ℃与 168.8 ℃。$[Zn(en)_3](FOX\text{-}7)_2$的热稳定性低于 $Zn(NH_3)_2(FOX\text{-}7)_2$。$[Zn(en)_3](FOX\text{-}7)_2$的撞击感度约为 20.6 J。

关键词： 结构化学；1,1-二氨基-2,2-二硝基乙烯(FOX-7)；锌化合物；晶体结构；热行为
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