Crystal structure, thermal decomposition mechanism and explosive properties of [Na(H$_2$TNPG)(H$_2$O)$_2$]$_n$

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Abstract

The new coordination polymer of sodium trinitrophloroglucinate, [Na(H$_2$TNPG)(H$_2$O)$_2$]$_n$, was synthesized by reacting trinitrophloroglucinol (H$_3$TNPG) with NaHCO$_3$ in aqueous solution and [Na(H$_2$TNPG)(H$_2$O)$_2$]$_n$ was recrystallized to be yellow single crystal. The title compound was characterized by using elemental analysis and Fourier transform infrared (FT-IR) spectrum. Its crystal structure was determined by single crystal X-ray diffraction analysis. The crystalline belongs to monoclinic system and $C2/c$ space group. Each Na$^+$ ion is six-coordinated to one H$_2$TNPG$^-$ anion and four water molecules in which the oxygen atoms in the water molecules act as bridging atoms. Coordination bonds, electrostatic interaction and intermolecular hydrogen bonds assemble the ions into network structures. The thermal decomposition mechanism of the complex was studied by using differential scanning calorimetry (DSC), thermogravimetry/derivative thermogravimetry (TG/DTG) and FT-IR techniques. Under nitrogen atmosphere with a heating rate of 10 °C/min the thermal decomposition of the complex contained one endothermic and five exothermic processes. Two intense exothermic decomposition processes were observed in the range of 173–228 °C suggesting its energetic nature and the solid decomposition residue at 500 °C was sodium isonitrile. Explosive properties revealed that the compound is sensitive to mechanical stimuli. All properties data observed show that the title compound has explosive properties and can act as components of ecologically clean initiating compositions.

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Keywords: Complex of sodium trinitrophloroglucinate; Molecular structure; Thermal decomposition mechanism; Explosive properties

1. Introduction

Many substances belonging to primary explosives group of energetic materials may be found among the chemical class of metallic salts of polynitro hydroxybenzenes. Some of these salts are of interest as promising ingredients of various pyrotechnic compositions. Among them are well known substances in service such as potassium picrate, barium and lead styphnates, and others [1–4]. 2,4,6-Trinitro-1,3,5-trihydroxybenzene (trinitrophloroglucinol, H$_3$TNPG) has been used in chemical industry as an ingredient for making dyes and explosive industry as an ingredient for priming composition, percussion caps and detonator formulations. Owing to the acidic nature of H$_3$TNPG, it

can form salts with a large number of metals as well as aromatic and aliphatic amines, which are also highly useful in initiating compositions. Unlike many salts of nitro derivatives of mono- and dihydroxybenzenes, which the structure, thermal decomposition and explosive properties are fairly known [5–10], metallic salts of H$_3$TNPG still remain poorly explored. Egorshev et al. [11] have reported the synthesis and the combustion behavior of metallic salts of H$_3$TNPG. The crystal structures of mono-, di- and tri-substituted potassium salts of trinitrophloroglucinol have been reported [12]. Crystal structure of any energetic compound is very important, as performance parameters such as high-velocity of detonation depends largely on density of material. Moreover, the sensitivity of an explosive depends on properties such as shear strength and molecular orientations of the crystalline material [13]. The research of the structure-properties relationship for the energetic materials is an object of permanent interest. We have studied the properties of H$_3$TNPG-salts of alkali metal because all of them are free of toxic heavy metals

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and can be recommended for further investigations as components of ecologically clean initiating compositions. In this paper, the authors reported the crystal structure, the thermal decomposition and explosive properties on the mono-substituted sodium complex of H_3TNPG, $[Na(H_2TNPG)(H_2O)_2]_n$, so as to deepen the studies on the H_3TNPG salts.

2. Experimental

2.1. Sample

H_3TNPG was prepared according to the literature method [14].

$[Na(H_2TNPG)(H_2O)_2]_n$ used in this work was prepared according to the following method: an appropriate amount of H_3TNPG was put into water, then stirred and the same equimolar sodium bicarbonate aqueous solution was added in a water bath at 70 °C. The yellow precipitate was collected by filtration, and dried in an oven. Single crystals suitable for X-ray measurement were obtained by recrystallization with the water at 0–5 °C. A yellow crystal with cross-dimensions of 0.46 mm × 0.46 mm × 0.20 mm was chosen for X-ray determination.

Elemental analysis for $C_6H_6N_3NaO_{11}$ (molar mass 319.13 g/mol) (%): calculated—C 22.56; N 13.16; H 1.88; found—C 22.23; N 13.52; H 1.91. IR (cm^{-1}, KBr pellets): 3159 m (v O–H), 1642s (v Ph–OH), 1481w (δ C=C), 1348s (v_s NO_2 and δ C–H), 889w, 785w, 727w (δ ring bone).

2.2. X-ray data collection and structure refinement

A suitable crystal (0.46 mm × 0.46 mm × 0.20 mm) was mounted on a normal-focus sealed tube, and placed on the goniometer of a Siemens P4 full automatic four-circle diffractometer. Unit cell parameters were determined by least squares analysis of 31 reflections with $5.72° < \theta < 12.99°$ using ω scans at 290 ± 2 K with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). 1168 reflections were collected between $2.32° < \theta < 25.47°$ yielding 1028 unique reflections ($R_{int} = 0.0108$). Information concerning crystallographic data collection and structure refinement is summarized in Table 1. Empirical absorption correction was applied to the intensity data.

The structure was solved by the direct methods routine of SHELXS-97 [15] with the space group $C2/c$, and subsequent difference-Fourier map revealed the positions of the remaining atoms. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL 97 [16], and all hydrogen atoms were treated isotropically. The atomic coordinates and displacement parameters, selected bond distances and angles are listed in Tables 2–4.

2.3. Physical techniques

Elemental analyses were performed on a Flash EA 1112 full-automatic trace element analyzer. The FT-IR spectra were recorded on a Bruker Equinox 55 spectrometer (KBr pellets) in the range of 4000–400 cm^{-1}. DSC and TG measurements

Table 1
Crystal data and structure refinement parameters for $[Na(H_2TNPG)(H_2O)_2]_n$

Empirical formula	$C_6H_6N_3NaO_{11}$
Molar mass (g/mol)	319.13
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	13.543(2)
b (Å)	12.358(2)
c (Å)	7.188(1)
β (°)	112.65(1)
V (Å^3)	1110.2(4)
Z	4
D_c (g/cm^3)	1.909
μ (Mo Kα) (mm^{-1})	0.218
F (0 0 0)	648
Crystal size (mm)	0.46 × 0.46 × 0.20
θ Range (°)	2.32–25.47
Measured reflections	1168
Independent reflections [$R_{int} = 0.0180$]	1028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0355, 0.0956
R_1, wR_2 (all data)	0.0482, 0.1007
δp_{max}, δp_{min} (e/Å^3)	0.294, −0.241

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[Na(H_2TNPG)(H_2O)_2]_n$

Atom	x	y	z	U(eq)
Na	0	428(1)	2500	52(1)
O(1)	0	7226(2)	2500	39(1)
O(2)	1833(1)	6914(1)	1739(3)	42(1)
O(3)	2739(1)	5891(2)	4241(3)	50(1)
O(4)	1822(1)	3962(1)	2717(3)	33(1)
O(5)	788(1)	2251(1)	2461(2)	34(1)
O(6)	801(1)	−879(1)	1190(3)	36(1)
N(1)	1902(1)	6167(1)	2900(3)	29(1)
N(2)	0	2774(2)	2500	26(1)
C(1)	0	6222(2)	2500	26(1)
C(2)	923(2)	5585(2)	2668(3)	24(1)
C(3)	945(2)	4475(2)	2642(3)	23(1)
C(4)	0	3891(2)	2500	23(1)

U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

Table 3
Bond distances (Å)

Na—O(6)	2.3369(19)	O(4)—H(4)	0.8240(10)
Na—O(6)#1	2.3369(19)	O(5)—N(2)	1.2570(18)
Na—O(5)	2.4972(18)	O(6)—Na#3	2.5116(18)
Na—O(5)#1	2.4972(18)	O(6)—H(6A)	0.8120(10)
Na—O(6)#2	2.5116(18)	O(6)—H(6B)	0.8150(10)
Na—O(6)#3	2.5116(18)	N(1)—C(2)	1.4610(2)
Na—N(2)	2.8990(3)	N(2)—O(5)#1	1.2570(18)
Na—Na#3	3.7464(9)	N(2)—C(4)	1.3810(4)
Na—Na#4	3.7464(9)	C(1)—C(2)	1.4420(2)
O(1)—C(1)	1.2410(3)	C(1)—C(2)#1	1.4420(2)
O(2)—N(1)	1.2240(2)	C(2)—C(3)	1.3730(3)
O(3)—N(1)	1.2210(2)	C(3)—C(4)	1.4380(2)
O(4)—C(3)	1.3290(2)	C(4)—C(3)#1	1.4380(2)

Symmetry transformations used to generate equivalent atoms—#1: $-x$, y, $-z + 1/2$; #2: x, $-y$, $z + 1/2$; #3: $-x$, $-y$, $-z$; #4: $-x$, $-y$, $-z + 1$.

Table 4
Bond angles (°)

O(6)—Na—O(6)#1	92.53(10)	O(6)#3—Na—Na#4	156.38(4)
O(6)—Na—O(5)	110.63(6)	N(2)—Na—Na#4	106.40(4)
O(6)#1—Na—O(5)	153.49(6)	Na#3—Na—Na#4	147.20(8)
O(6)—Na—O(5)#1	153.49(6)	C(3)—O(4)—H(4)	108.00(2)
O(6)#1—Na—O(5)#1	110.63(6)	N(2)—O(5)—Na	95.37(12)
O(5)—Na—O(5)#1	51.15(7)	Na—O(6)—Na#3	101.13(6)
O(6)—Na—O(6)#2	120.01(7)	Na—O(6)—H(6A)	109.00(2)
O(6)#1—Na—O(6)#2	78.87(6)	Na#3—O(6)—H(6A)	116.00(2)
O(5)—Na—O(6)#2	78.40(6)	Na—O(6)—H(6B)	117.00(3)
O(5)#1—Na—O(6)#2	78.49(6)	Na#3—O(6)—H(6B)	104.00(3)
O(6)—Na—O(6)#3	78.40(6)	H(6A)—O(6)—H(6B)	110.00(3)
O(6)#1—Na—O(6)#3	120.01(7)	O(3)—N(1)—O(2)	123.58(19)
O(5)—Na—O(6)#3	78.49(6)	O(3)—N(1)—C(2)	118.62(18)
O(5)#1—Na—O(6)#3	78.40(6)	O(2)—N(1)—C(2)	117.80(17)
O(6)#2—Na—O(6)#3	154.34(9)	O(5)#1—N(2)—O(5)	118.10(2)
O(6)—Na—N(2)	133.74(5)	O(5)#1—N(2)—C(4)	120.95(11)
O(6)#1—Na—N(2)	133.74(5)	O(5)—N(2)—C(4)	120.95(11)
O(5)—Na—N(2)	25.58(3)	O(5)#1—N(2)—Na	59.05(11)
O(5)#1—Na—N(2)	25.58(3)	O(5)—N(2)—Na	59.05(11)
O(6)#2—Na—N(2)	77.17(5)	C(4)—N(2)—Na	180.0(2)
O(6)#3—Na—N(2)	77.17(5)	O(1)—C(1)—C(2)	123.08(12)
O(6)—Na—Na#3	41.13(4)	O(1)—C(1)—C(2)#1	123.08(12)
O(6)#1—Na—Na#3	111.27(7)	C(2)—C(1)—C(2)#1	113.8(2)
O(5)—Na—Na#3	94.93(5)	C(3)—C(2)—C(1)	124.56(19)
O(5)#1—Na—Na#3	115.05(5)	C(3)—C(2)—N(1)	118.05(18)
O(6)#2—Na—Na#3	156.38(4)	C(1)—C(2)—N(1)	117.38(18)
O(6)#3—Na—Na#3	37.74(4)	O(4)—C(3)—C(2)	119.99(18)
N(2)—Na—Na#3	106.40(4)	O(4)—C(3)—C(4)	121.42(18)
O(6)—Na—Na#4	111.27(7)	C(2)—C(3)—C(4)	118.58(19)
O(6)#1—Na—Na#4	41.13(5)	N(2)—C(4)—C(3)	120.09(12)
O(5)—Na—Na#4	115.05(5)	N(2)—C(4)—C(3)#1	120.09(12)
O(5)#1—Na—Na#4	94.93(5)	C(3)—C(4)—C(3)#1	119.8(2)
O(6)#2—Na—Na#4	37.74(4)		

were carried out using Perkin-Elmer Pyris-1 differential scanning calorimeter and thermogravimetric balance, respectively, using dry nitrogen as atmosphere with a pressure of 0.2 MPa. The crystal samples were sealed in aluminum pans for DSC experiments and held in platinum pans for TG experiments, and were heated with a linear heating rate with 5, 10, 15, 20 and 25 °C/min from 50 to 500 °C. The impact sensitivity was determined by Fall Hammer Method using 0.8 kg drop weight and friction sensitivity was determined on MGY-1 pendular friction sensitivity apparatus by following a standard method [17].

3. Results and discussion

3.1. Molecular structure

The molecular structure of $[Na(H_2TNPG)(H_2O)_2]_n$ was determined by X-ray single crystal diffraction. The molecule structure and atomic numbering of the complex are showed in Fig. 1. The structure is built up from isolated H_2TNPG^- anions and Na^+ cations. The adjacent molecules form a chain wherein the crystal waters act as bridging molecules between cations. The center metal Na atom is six-coordinated in a roughly octahedral geometry by four oxygen atoms coming from four H_2O molecules (O(6), O(6)#1, O(6)#2, O(6)#3) and two oxygen atoms (O(5) and O(5)#1) on one nitro group of one H_2TNPG^-,
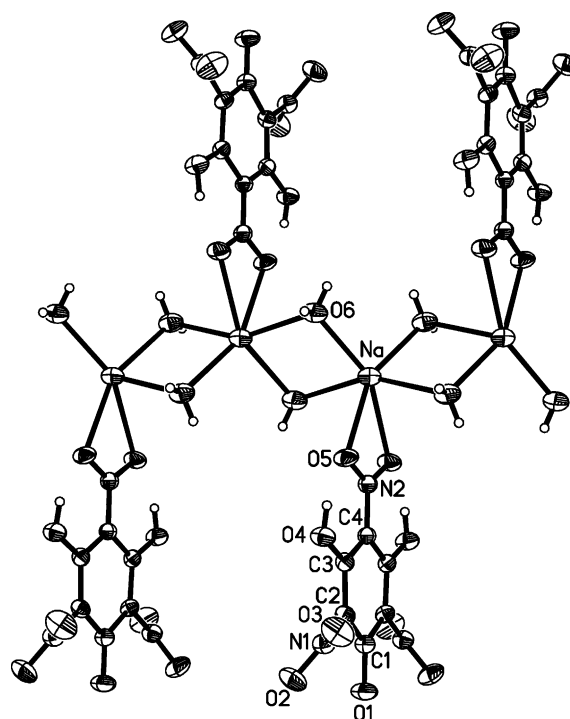

Fig. 1. The molecular structure and atomic numbering scheme of $[Na(H_2TNPG)(H_2O)_2]_n$.

and help to bridge the cell units in the chain, along with the shared water molecules. Each metal Na takes part in three four-membered chelate rings formed. These rings are not in a plane, but each ring is coplanar. The packing of the molecule in the lattice is illustrated in Fig. 2. The net structure of three-dimensional infinite layer is formed through coordination bonds, electrostatic interaction and hydrogen bonds.

H_3TNPG is an acidic compound when it reacts with NaHCO$_3$, O(1)H on the benzene ring gives its H^+ ion out, and forms a univalent anion. Na^+ ion acts with H_2TNPG^- through coordinating with nitro group and a part of electrostatic attraction, which result in that $[Na(H_2TNPG)(H_2O)_2]_n$ is more stability. Figs. 1 and 2 show that all H_2TNPG^- anions are bidentates. Nitro group coordinated with the Na atom is coplanar with the phenyl ring and is conjugation with the ring, but two other nitro groups are not coplanar. There is a special π_3^4 bond in the coordination nitro group, which plays a significant role to complex stability. Owing to the p–π conjugation between atoms of phenolic hydroxyl group and phenyl ring, the bond distance of O(1)–C(1) is 1.241(3) Å, which is a very close approximation to the value of natural double bond C=O(1.210 Å) [18].

Tables 3 and 4 report selected bond distances and angles for the title compound, respectively. In the molecule, the Na–O distances are in a range of 2.3369–2.5116 Å, with an average length of 2.4486 Å, which is slightly shorter than corresponding average distance 2.388 Å [19]. The symmetry related O(6) and O(6)#1 water oxygen, which are bridging the sodium centers with identical separations (2.5116(18) Å), are involved in an intricate hydrogen bonding network. In particular, the strong hydrogen bonding interactions are as shown at Table 5: O(6)···O(1) 2.887(2); O(6)···O(4) 3.011(2) Å. The hydroxylic
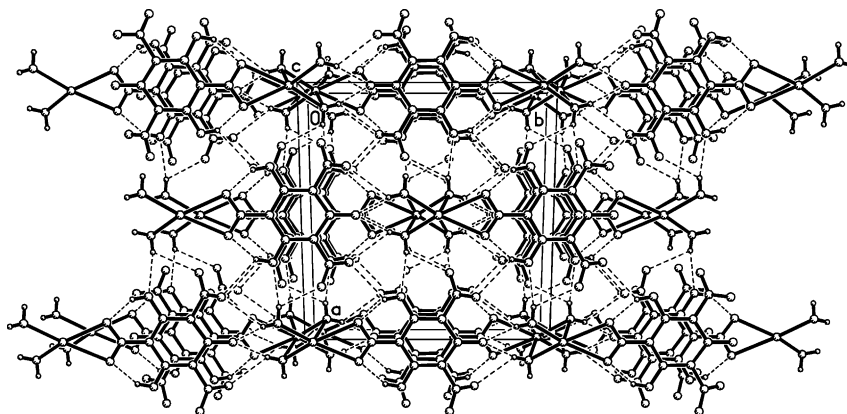
Fig. 2. The packing arrangement of $[Na(H_2TNPG)(H_2O)_2]_n$.

Table 5
Hydrogen bond distances (Å) and angles (°)

D	H	A	D—H	H···A	D···A	D—H···A
O4	H4	O5	0.824(10)	1.764(18)	2.504(2)	148(3)
O6	H6A	O1	0.812(10)	2.097(13)	2.887(2)	164(3)
O6	H6B	O4	0.815(10)	2.208(13)	3.011(2)	168(4)

proton of hydroxyl group at C(3) is bonded to O atom of nitro-group at C(4) through an intra hydrogen bonding, and a steady-going aberrance six-membered ring is formed by hydrogen bond: O(4)–H(4)–O(5)–N(2)–C(4)–C(3).

3.2. Thermal decomposition mechanism

The DSC and TG/DTG curves under the linear heating rate of 10 °C/min with nitrogen atmosphere are shown in Figs. 3 and 4 to demonstrate the thermal decomposition processes of $[Na(H_2TNPG)(H_2O)_2]_n$. There are one endothermic peak and five exothermic peaks in the DSC curves: two are sharp peaks, and others are much weaker subsequent peaks.

The first endothermic peak starts at 65 °C and ends at 90 °C in the DSC curves. The TG curves shows that during heating of $[Na(H_2TNPG)(H_2O)_2]_n$ the weight loss. Corresponding to this temperature range is 10.8 wt%, which roughly coincides with the value of 11.3 wt%, calculated for the loss of two water molecules from the complex.
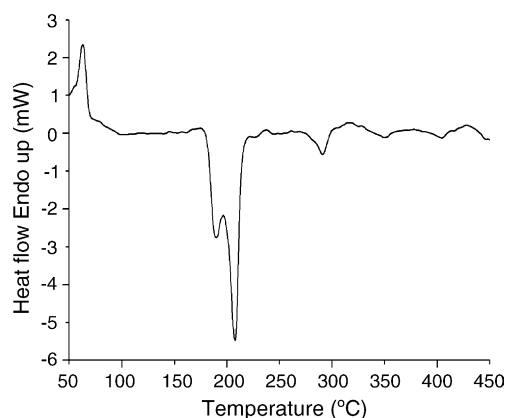
Further decomposition of the dehydrated complex occurs at 173–228 °C. There are two intense exothermic peaks in the DSC curves: the first peak temperature is 189 °C, the other peak temperature is 208 °C. Because two intense exothermic decomposition processes occur successively, one decomposition process does not finish, and anther occurs. The exothermic peak cannot be separated, which form a wide exothermic peak. Corresponding to two exothermic processes, there is a mass loss of 49.2% on the TG curve in the temperature range of 173–228 °C, and the maximum rate of mass loss of 28.3%/min is observed at 208 °C. The total exothermic enthalpy of two processes is 1618.95 kJ/mol. The IR spectrum of solid residue at 230 °C was performed using FT-IR. The absorption at 2213 cm^{-1} indicates the existence of –N=C=O [8,9], which is the asymmetric stretch vibration ν_{as}(–N=C=O). At the same time, the very strong absorption at 1632 cm^{-1} may be attributed to the asymmetric stretch vibration ν_{as}(RCO$_2^-$). By analyzing the decomposition temperature of the two processes, we can know that the probable thermal decomposition mechanism is the elimination of nitro-group followed by a breakdown of H$_2$TNPG$^-$ ring on heating.

A third exothermic peak occurs intensely between 279 and 308 °C and the peak temperature is 298 °C with a lower enthalpy change of 191.41 kJ/mol. This process is accompanied by a mass
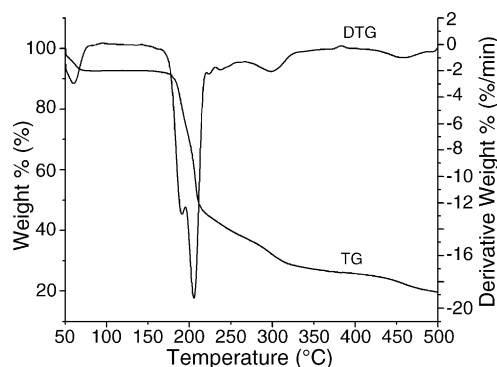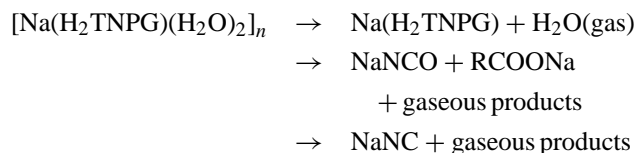

Fig. 3. The DSC curve of $[Na(H_2TNPG)(H_2O)_2]_n$ under N$_2$ atmosphere with a heating rate of 10 °C/min.

Fig. 4. The TG/DTG curves of $[Na(H_2TNPG)(H_2O)_2]_n$ under N$_2$ atmosphere with a heating rate of 10 °C/min.

loss of 12.7% in the temperature range of 264–312 °C and the maximum rate of mass loss is at 295 °C.

On the TG curve, there still is a slow mass loss of 9.3% from 320 to 500 °C. When temperature is up to 500 °C, the residue amounts to 18.5% under a nitrogen atmosphere, which is substantial solid residue comparing with the decomposition of $K(NTO)(H_2O)$, KPA, $K_2(TNR)(H_2O)$ and $K(HTNR)(H_2O)$ [7,5,8,9]. The IR spectrum of solid residue at 500 °C was also performed using FT-IR. The absorption at 2170 cm^{-1} indicates the existence of $-N\equiv C$, and the characteristic bands of $-N=C=O$ and $RCOO^-$ disappear.

In a word, the thermal decomposition processes of $[Na(H_2TNPG)(H_2O)_2]_n$ can be displayed with the following illustration according to our above work:

$$[Na(H_2TNPG)(H_2O)_2]_n \quad \rightarrow \quad Na(H_2TNPG) + H_2O(gas)$$
$$\rightarrow \quad NaNCO + RCOONa$$
$$+ \text{gaseous products}$$
$$\rightarrow \quad NaNC + \text{gaseous products}$$

3.3. Non-isothermal kinetics analysis

In the present work, Kissinger's method [20] and Ozawa–Doyle's method [21,22] are widely used to determine the apparent activation energy (E) and the pre-exponential factor (A). The Kissinger and Ozawa–Doyle equations are as follows, respectively:

$$\frac{\mathrm{d}\ln\frac{\beta}{T_P^2}}{\mathrm{d}\frac{1}{T_P}} = -\frac{E}{R} \tag{1}$$

$$\log\beta + \frac{0.4567E}{RT_P} = C \tag{2}$$

where T_P is the peak temperature, A the pre-exponential factor, E the apparent activation energy, R the gas constant, β the linear heating rate and C is constant.

Although the thermal decomposition of $[Na(H_2TNPG)(H_2O)_2]_n$ is complex, Kissinger's and Ozawa–Doyle's method were applied to study the kinetics parameters, based on the first exothermic peak temperatures measured at five different heating rates of 5, 10, 15, 20 and 25 °C/min. From the original data, the apparent activation energy E_k and E_o, pre-exponential factor A_k and linear coefficient R_k and R_o were determined and shown in Table 6.

3.4. Sensitivity test

One of the most important parameter in the development and manufacture of new primary explosives compositions is assessing the safety of store to accidental ignition. Primarily sensitivity is a measure of the response of the composition to external stimuli as impact, friction, heat, static charge, etc.

Impact sensitivity was determined by Fall Hammer Apparatus using 0.8 kg drop weight and 20 mg sample. The height corresponding to 50% probability of explosion was calculated.

Table 6
The peak temperatures of the first exotherm at different heating rates and the chemical kinetics parameters

Heating rates (°C/min)	Peak temperatures (°C)
5	181.8
10	189.4
15	192.8
20	196.4
25	198.8
The calculation results by Kissinger's method	
E_k (kJ/mol)	162.6
$\log A_k$ (s^{-1})	16.56
Linear correlation coefficient (R_k)	0.9988
The calculation results by Ozawa–Doyle's method	
E_o (kJ/mol)	161.9
Linear correlation coefficient (R_o)	0.9989

Twenty milligrams of $[Na(H_2TNPG)(H_2O)_2]_n$ was compacted to copper cap under the press of 39.2 MPa, and was hit by 0.8 kg drop hammer. The 50% firing high is 12.41 cm, which is higher than that of lead azide (10.03 cm) [23].

Friction sensitivity was determined using 20 mg sample. When $[Na(H_2TNPG)(H_2O)_2]_n$ was compressed between two steel poles with mirror surfaces at the pressure of 1.23 MPa, and was hit horizontally with a 1 kg hammer from 70° angle, the firing rate is 68%, which is higher than the value of potassium 7-hydroxy-4,6-dihydrobenzofuroxan (KDNBF, 41%) [24].

The study of sensitivity test reveals the title compound has sensitive nature towards impact and friction. It is showed that it has explosive property and can act as components of initiating compositions.

4. Conclusion

The sodium trinitrophloroglucinate, $[Na(H_2TNPG)(H_2O)_2]_n$, has been synthesized and characterized. Its crystal structure belongs to monoclinic system and crystal structure data: $C2/c$ space group, $a = 13.543(2)$ Å, $b = 12.358(2)$ Å, $c = 7.188(1)$ Å, $\beta = 112.65(1)°$. The center metal Na atom is six-coordinated in a roughly octahedral geometry by four oxygen atoms coming from four H_2O molecules and two oxygen atoms on one nitro group of one H_2TNPG^-, and help to bridge the cell units in the chain, along with the shared water molecules. The net structure of three-dimensional infinite layer is formed through coordination bonds, electrostatic interaction and hydrogen bonds. Thermolysis indicated the two intense exothermic decomposition of $[Na(H_2TNPG)(H_2O)_2]_n$ in the temperature range of 173–228 °C, and the final decomposed residue at 500 °C contains sodium isonitrile. The sensitivity experimental results indicate that $[Na(H_2TNPG)(H_2O)_2]_n$ has explosive properties.

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