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三硝基间苯三酚 5-氨基四唑盐的晶体结构及热分解

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摘要: 制备得到标题化合物并对其进行了元素分析与红外光谱分析。用 X 射线衍射方法测得其晶体结构属于正交晶系, 空间群 *Pbca*, 晶胞参数 $a=0.6624(2)$ nm, $b=1.7933(4)$ nm, $c=2.3117(5)$ nm, $V=2.7458(9)$ nm³, $Z=4$, $D_c=1.849$ g·cm⁻³。其分子式可写作(ATZ)TNPG·2H₂O。5-氨基四唑阳离子(ATZ⁺)和三硝基间苯三酚阴离子(TNPG⁻)通过氢键在 *b* 轴和 *c* 轴方向上联成二维层面, 然后在 *a* 轴方向通过不同层中的水分子之间的氢键联接起来。用差示扫描量热法(DSC), TG-DTG 结合傅立叶变换红外光谱(FT-IR)分析了其热分解过程。在氮气气氛下用 10 °C·min⁻¹ 的升温速率测定发现, 该化合物经历一个峰温为 76 °C 的吸热过程及一个峰温为 203 °C 的放热过程。前者为脱除结晶水的过程, 后者为产物中的 TNPG⁻与 ATZ⁺的热分解过程, 放热的焓变为-212.10 kJ·mol⁻¹。对该过程估算动力学参数: 采用 Kissinger 法得活化能 $E=132.1$ kJ·mol⁻¹, $\ln(A/s^{-1})=12.54$, $r=0.9990$; 采用 Ozawa-Doyle 法得 $E=133.1$ kJ·mol⁻¹, $r=0.9992$ 。

关键词: 三硝基间苯三酚; 5-氨基四唑; TNPG; 制备; 晶体结构; 热分解

中图分类号: O641; O642; O741+6

Crystal Structure and Thermal Decomposition of 5-Aminotetrazole Trinitrophenolglucinate

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Abstract: 5-Aminotetrazole trinitrophenolglucinate ((ATZ) TNPG) was prepared and characterized by elemental analysis and FT-IR spectroscopy. The crystal structure was determined by X-ray diffraction analysis and it belonged to orthorhombic system and *Pbca* space group with $a=0.6624(2)$ nm, $b=1.7933(4)$ nm, $c=2.3117(5)$ nm, $V=2.7458(9)$ nm³, $Z=4$, and $D_c=1.849$ g·cm⁻³. The molecular formula was confirmed to be (ATZ)TNPG·2H₂O. 5-Aminotetrazole cation (ATZ⁺) and trinitrophenolglucinate anion (TNPG⁻) were linked into 2-D layers along *b*-axis and *c*-axis by hydrogen bonds. Then the layers were linked along *a*-axis by hydrogen bonds between the water molecules belonging to different layers. The thermal decomposition mechanism of the compound was studied by differential scanning calorimetry (DSC), thermogravimetry-thermogravimetric analysis (TG-DTG), and Fourier transform-infrared (FT-IR) spectroscopy techniques. Under nitrogen atmosphere with a heating rate of 10 °C·min⁻¹, the compound experienced one endothermic process with peak temperature of 76 °C and one exothermal process with peak temperature of 203 °C. The former was confirmed to be a dehydrate process. The latter was the decomposition of TNPG⁻ and ATZ⁺ in the compound. The

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exothermic enthalpy change of this process was $-212.10 \text{ kJ} \cdot \text{mol}^{-1}$. The kinetic parameter calculation from Kissinger's method were, $E=132.1 \text{ kJ} \cdot \text{mol}^{-1}$, $\ln(A/s^{-1})=12.54$ with $r=0.9990$, and the calculation results from Ozawa-Doyle's method were, $E=133.1 \text{ kJ} \cdot \text{mol}^{-1}$ with $r=0.9992$.

Key Words: Trinitrophenolroglucinol; ATZ; TNPG; Preparation; Crystal structure; Thermal decomposition

Aminotetrazoles are prospective materials for the generation of gases, as blowing agents, solid propellants, and other combustible and thermally decomposing systems for their perfect properties. As a kind of the most important aminotetrazoles, 5-aminotetrazole (ATZ) and its derivatives have been widely investigated recently^[1-9]. The cadmium complex with 5-aminotetrazole as ligand was synthesized and characterized by instrumental analysis, and its crystal structure was determined by X-ray diffraction analysis in Ref. [10]. The complex Cs (ATZ) was prepared by reacting ATZ as an acid with aqueous solution of CsOH^[11]. ATZ is also used as an alkali to synthesize its nitrate salt or hydrohalide salt^[15,12]. (ATZ)NO₃ was used as an ingredient of gas-generating composite propellants^[5]. These kinds of gas generators were superior to those ammonium nitrate gas generators used earlier because they possessed better burning rate, increased temperature stability, higher non-corrosive gas volumes, a minimum of solid particulates, and lower flame temperatures^[5-8].

2,4,6-trinitro-1,3,5-trihydroxybenzene (trinitrophenolroglucinol, TNPG) is a strong acidic organic compound with three nitro-groups and three phenolic hydroxyl groups conjugated with the ring^[13-19]. It is also an important explosive. The metallic salts of TNPG have been studied to be used as pyrotechnic compositions. The lead salt of TNPG has been extensively studied and recommended for using as an initiating explosive^[20]. But till now, no reports about the product of ATZ reacting with TNPG have been found. The present work is the synthesis and characterization of this compound.

1 Experimental

1.1 Preparation and characterization

The raw ATZ was prepared following a literature method^[21], whereas the raw TNPG was prepared by the method given in previous literature^[17].

The title compound was prepared by reacting ATZ with TNPG in deionised water in the 1:1 molar ratio. The reaction temperature and reaction time were controlled. The yellow single crystal of the compound, suitable for X-ray diffraction study, was cultured from the aqueous solution of the product by a slow evaporation method at the culture box at 25 °C for 7 days.

The elements of C, H, and N were determined by a Flash EA 1112 full-automatic trace element analyzer. Analysis found (cal.): C 22.21% (22.00%), H 2.56% (2.64%), and N 29.15% (29.32%). The experimental results are close to the calculated values. The chemical formula of the title compound can be written as C₁₄H₂₀N₁₆O₂₂, based on the result.

The new compound was characterized by FT-IR spectra using

a Bruker Equinox 55 FTIR spectrophotometer on KBr pellets in the range of 4000–400 cm⁻¹ with the resolution of 4 cm⁻¹. Most of the vibration peaks of the main infrared absorption bands were assigned as follows^[15,17,21] (cm⁻¹): 3617 (m, $\nu_{\text{O-H}}$), 3477 (m, $\nu_{\text{asN-H}}$), 3325 (m, $\nu_{\text{sN-H}}$), 3235 (m, $\nu_{\text{N-H}}$), 1704 ($\delta_{\text{-NH}_2}$), 1625 ($\delta_{\text{-NH}}$), 1503 ($\delta_{\text{C-C}}$), 1309 (ν_{sNO_2}), 1171 ($\delta_{\text{C-O}}$), 915 ($\delta_{\text{ring bone}}$), 792 ($\delta_{\text{ring bone}}$), 707 ($\delta_{\text{ring bone}}$), and 542 ($\delta_{\text{ring bone of ATZ}}$).

1.2 X-ray data collection and structure refinement

A block crystal with three dimensions of 0.12 mm×0.10 mm×0.04 mm was selected for X-ray analysis. The X-ray diffraction data were collected on a Rigaku MicroMax-007 diffractometer equipped with a Saturn 70 CCD using Mo K_α radiation ($\lambda=0.071073 \text{ nm}$) at 293(2) K in the ω scans mode. Cell parameters were determined in the θ range of 1.76°–27.90°. Lorentz polarization and empirical absorption correction were applied to the raw intensities. All non-hydrogen atoms were obtained from the difference Fourier map and refined anisotropically. The hydrogen atoms were obtained geometrically and treated as riding on the parent atoms or were constrained in the locations during re-

Table 1 Crystal data and structure refinement for ATZ(TNPG)·2H₂O

Item	Value
CCDC	668253
empirical formula	C ₁₄ H ₂₀ N ₁₆ O ₂₂
formula weight	764.46
<i>T</i> /K	293(2)
λ /pm	71.073
crystal system	orthorhombic
space group	<i>Pbca</i>
<i>a</i> /nm	0.6624(2)
<i>b</i> /nm	1.7933(4)
<i>c</i> /nm	2.3117(5)
<i>V</i> /nm ³	2.7458(9)
<i>Z</i>	4
calculated density (mg·cm ⁻³)	1.849
absorption coefficient (mm ⁻¹)	0.175
<i>F</i> (000)	1568
crystal size (mm)	0.12×0.10×0.04
θ range for data collection	1.76° to 27.90°
limiting indices	$-7 \leq h \leq 8$, $-23 \leq k \leq 14$, $-30 \leq l \leq 30$
reflections collected/unique	19884/3280 [<i>R</i> (int)=0.0523]
absorption correction	semi-empirical from equivalents
max. and min. transmissions	0.9930 and 0.9793
refinement method	full-matrix least-squares on <i>F</i> ²
data/restraints/parameters	3280/12/270
goodness-of-fit on <i>F</i> ²	1.129
final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)	<i>R</i> ₁ =0.0448, <i>wR</i> ₂ =0.1106
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0529, <i>wR</i> ₂ =0.1165
extinction coefficient	0.003(2)
largest diff. peak and hole (e ⁻ ·nm ⁻³)	351 and -293

finements. Information of crystallographic data collection and structure refinement is summarized in Table 1.

1.3 Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on Perkin-Elmer Pyris-1 differential scanning calorimeter and thermogravimetric analyzer, respectively, using dry oxygen free nitrogen as atmosphere with a flowing rate of $20 \text{ mL} \cdot \text{min}^{-1}$. About 0.5 mg of the sample was sealed in aluminum pans for DSC with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ from 50 to $450 \text{ }^\circ\text{C}$. About 0.5 mg of the sample was held in platinum pans for TG with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ from 50 to $450 \text{ }^\circ\text{C}$.

2 Results and discussion

2.1 Crystal structure of (ATZ)TNPG·2H₂O

The selected bond lengths and bond angles as well as the hydrogen bond lengths and angles are given in Tables 2 to 4. The molecular structure and packing arrangement of the title compound are shown in Figs.1 and 2, respectively.

There are an ATZ cation, a TNPG anion, and two water

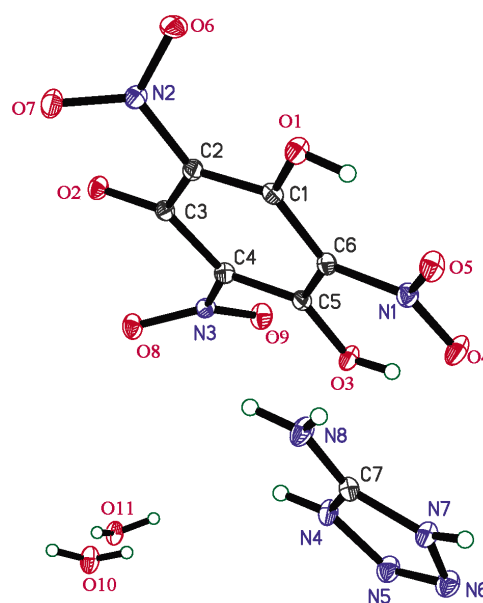


Fig.1 Molecular structure and atomic numbering scheme for (ATZ)TNPG·2H₂O

molecules in the asymmetric unit according to the structure analysis. The molecular formula of the title compound was determined as (ATZ)TNPG·2H₂O. It can be seen in Fig.1 that the proton of one hydroxyl group of TNPG linked to C3 transfers to N4 (or N7) but not to the amino groups of the ATZ molecule. This is similar to the 1,5-diaminotetrazole reacting with the picric acid^[9]. The molecule becomes completely symmetrical as a whole.

Though there are three H⁺ ions that can be dissociated from three hydroxyl groups of the TNPG molecule theoretically, it is found that only one of the hydroxyl groups can be substituted by ATZ experimentally. To investigate the reason, the stepwise dissociation constants of TNPG were determined to be $\text{p}K_1=0.02$, $\text{p}K_2=3.6$, and $\text{p}K_3=7.2$ by potentiometric titration method. The

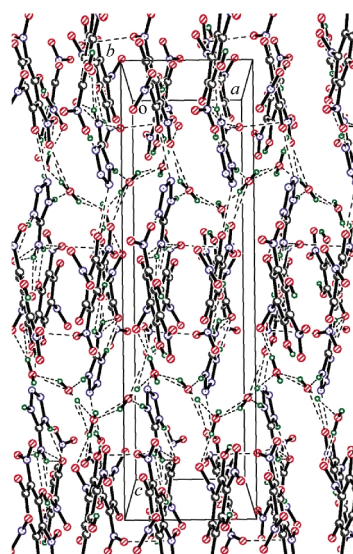


Fig.2 Packing diagram of (ATZ)TNPG·2H₂O crystal along b-axis with 50% probability

Table 2 Selected bond lengths (*l*) for (ATZ)TNPG·2H₂O

Bond	<i>l</i> /nm	Bond	<i>l</i> /nm
O(1)—C(1)	0.1324(8)	O(7)—N(2)	0.1230(8)
O(2)—C(3)	0.1248(8)	O(8)—N(3)	0.1241(7)
O(3)—C(5)	0.1316(8)	O(9)—N(3)	0.1223(8)
O(4)—N(1)	0.1249(8)	N(4)—C(7)	0.1334(9)
O(5)—N(1)	0.1252(7)	N(7)—C(7)	0.1335(9)
O(6)—N(2)	0.1243(7)	N(8)—C(7)	0.1319(9)

Table 3 Selected bond angles (θ) for (ATZ)TNPG·2H₂O

Bond	θ ($^\circ$)	Bond	θ ($^\circ$)
O(4)—N(1)—C(6)	120.6(6)	N(6)—N(5)—N(4)	107.4(6)
O(5)—N(1)—C(6)	120.2(6)	N(5)—N(6)—N(7)	108.6(6)
O(7)—N(2)—C(2)	119.8(5)	N(5)—N(4)—H(4A)	127.0(7)
O(6)—N(2)—C(2)	118.4(6)	N(6)—N(7)—H(7A)	118.0(8)
O(9)—N(3)—C(4)	119.0(5)	C(7)—N(8)—H(8A)	121.0(5)
O(8)—N(3)—C(4)	118.1(6)	C(7)—N(8)—H(8B)	123.0(6)
C(7)—N(4)—N(5)	110.2(6)	N(8)—C(7)—N(4)	126.2(7)
C(7)—N(7)—N(6)	108.6(6)	N(8)—C(7)—N(7)	128.7(6)

Table 4 Hydrogen bonds for (ATZ)TNPG·2H₂O

D—H···A	<i>l</i> _{D—H} /nm	<i>l</i> _{H···A} /nm	<i>l</i> _{D···A} /nm	$\theta_{\text{D—H}\cdots\text{A}}$ ($^\circ$)
O(1)—H(1)···O(5)	0.08200	0.17800	0.2501(7)	146.00
O(3)—H(3)···O(4)	0.08200	0.17800	0.2501(8)	146.00
N(4)—H(4A)···O(2)#3	0.090(3)	0.201(7)	0.2743(3)	139(6)
N(7)—H(7A)···O(11)#4	0.092(6)	0.167(8)	0.2577(8)	169(13)
N(8)—H(8A)···O(8)#3	0.089(3)	0.211(7)	0.2879(3)	145(7)
N(8)—H(8B)···O(6)#5	0.088(4)	0.208(6)	0.2920(3)	158(9)
O(10)—H(10A)···N(5)#6	0.086(3)	0.234(8)	0.3193(3)	176(15)
O(10)—H(10B)···O(9)#8	0.087(5)	0.230(8)	0.3058(3)	147(9)
O(11)—H(11A)···O(10)	0.086(9)	0.210(1)	0.2846(3)	154(9)
O(11)—H(11B)···O(4)#9	0.087(9)	0.251(9)	0.2920(7)	110(7)

symmetry operation: #3) $-1/2+x, 1/2-y, 1-z$; #4) $-1+x, -1+y, z$; #5) $1-x, -y, 1-z$; #6) $1-x, 1/2+y, 1/2-z$; #8) $3/2-x, 1/2+y, z$; #9) $1/2+x, 1+y, 1/2-z$

pH of ATZ solution was tested to be 2 to 4 by Ref.[21], so the second H^+ ion of TNPG can not be deprived by ATZ.

All the atoms except a nitro group are coplanar in the TNPG molecule^[17]. But in $(ATZ)(TNPG) \cdot 2H_2O$, two protons of two hydroxyl groups are bonded to O atom of their common neighboring nitro groups (**a**) (bonded to C6) by hydrogen bonds. The torsion angles of two other nitro groups (**b**) (bonded to C2), and (**c**) (bonded to C4) relative to the aromatic ring are 39.7° and 41.3° , respectively. The nitro group (**a**) is bonded to O atom of a water molecule by intermolecular hydrogen bond and bonded to hydroxyl groups by intramolecular hydrogen bonds. The nitro group (**b**) is bonded to $-NH-$ group of one ATZ cation, $-NH_2$ group of another ATZ cation, and a water molecule by intermolecular hydrogen bonds. The nitro group (**c**) is bonded to the hydroxyl group of another neighboring TNPG anion and a water molecule by intermolecular hydrogen bonds. Each TNPG anion is surrounded by three ATZ cations, whereas each ATZ cation is surrounded by three TNPG anions. The water molecules disperse in the interspaces of them. ATZ cations and TNPG anions were linked into 2-D layers along *b*-axis and *c*-axis by hydrogen bonds between $-NH_2$, $-NH$, and $-NO_2$, $-O$. Then the layers were linked along *a*-axis by hydrogen bonds between water molecules belonging to different layers (Fig.2).

2.2 Thermal decomposition of $(ATZ)TNPG \cdot 2H_2O$

The thermal decomposition of the title compound was investigated by DSC and TG-DTG. The curves are shown in Fig.3 and Fig.4, respectively.

The DSC curve shows that there are one endothermic process and one intense exothermic process. At a heating rate of $10^\circ C \cdot min^{-1}$, the endothermic process starts at $61^\circ C$ and ends around $125^\circ C$ with a peak temperature of $76^\circ C$. The corresponding mass loss is about 9.38% in the TG-DTG curve. Because the calculated mass percent of the water molecules in the title compound is 9.43%, this endothermic process can be assigned to the loss of water molecules. And the endothermic enthalpy change of this process is $106.51 kJ \cdot mol^{-1}$.

The exothermic process starts at $183^\circ C$ and ends around $225^\circ C$ with peak temperature of $203^\circ C$. The mass loss in this process is 43.34%, the total mass loss is 67.41%, and the final residue content is 32.59%. The exothermic enthalpy change of

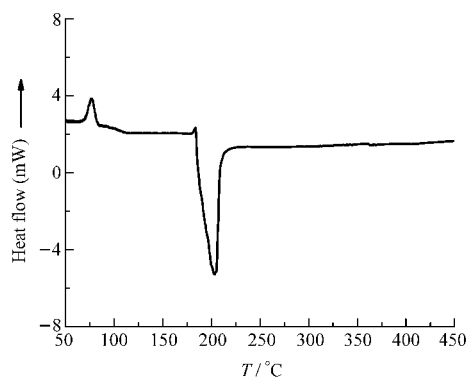


Fig.3 DSC curve of $(ATZ)TNPG \cdot 2H_2O$

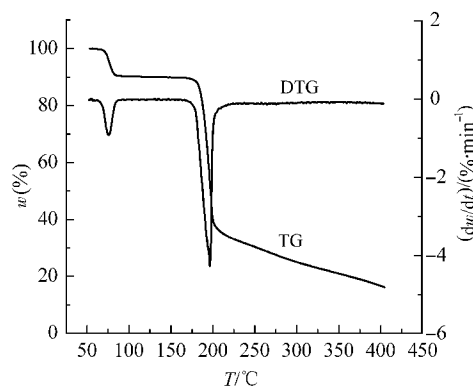


Fig.4 TG-DTG curves of $(ATZ)TNPG \cdot 2H_2O$

this process is $-212.10 kJ \cdot mol^{-1}$. The decomposition of the title compound has only one exothermic process, and the decomposition temperature is lower than that of $(ATZ)NO_3$. These are good properties for developing a gas generator agent.

Kissinger's method and Ozawa-Doyle's method were used to estimate the kinetic parameters, based on the exothermic peak temperatures measured at different heating rates^[22,23]. The calculation results from Kissinger's method are, $E=132.1 kJ \cdot mol^{-1}$ and $\ln(A/s^{-1})=12.54$ with $r=0.9990$, and the calculation results from Ozawa-Doyle's method are, $E=133.1 kJ \cdot mol^{-1}$ with $r=0.9992$.

3 Conclusions

The new compound $(ATZ)TNPG \cdot 2H_2O$ is an ionic compound made up of an ATZ cation, a TNPG anion, and two crystal water molecules. The existence of complicated hydrogen bond networks and electrostatic attraction between cation and anion that lead to the title compound has better stability. Thermal analysis showed that the title compound had good behavior. This makes the compound a promising ingredient of the gas-generating formula.

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