



Original article

Synthesis, crystal structure and thermal behavior of 4-amino-3,5-dinitropyrazole copper salt



Ying-Lei Wang, Feng-Qi Zhao*, Yue-Ping Ji, Jian-Hua Yi, Ting An, Wei-Xiao Liu

Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

ARTICLE INFO

Article history:

Received 1 December 2013

Received in revised form 11 December 2013

Accepted 19 December 2013

Available online 9 January 2014

Keywords:

Physical chemistry

4-Amino-3,5-dinitropyrazole copper salt

Energetic combustion catalyst

Crystal structure

Thermal behavior

ABSTRACT

A novel energetic combustion catalyst, 4-amino-3,5-dinitropyrazole copper salt ($[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$), was synthesized in a yield of 93.6% for the first time. The single crystal of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$ was determined by single crystal X-ray diffraction. It crystallizes in a triclinic system, space group $P\bar{1}$ with crystal parameters $a = 5.541(3) \text{ \AA}$, $b = 7.926(4) \text{ \AA}$, $c = 10.231(5) \text{ \AA}$, $\beta = 101.372(8)^\circ$, $V = 398.3(3) \text{ \AA}^3$, $Z = 1$, $\mu = 1.467 \text{ mm}^{-1}$, $F(000) = 243$, and $D_c = 2.000 \text{ g cm}^{-3}$. The thermal behavior and non-isothermal decomposition reaction kinetics of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$ were studied by means of different heating rate differential scanning calorimetry (DSC). The kinetic equation of major exothermic decomposition reaction for $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$ was obtained. The entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), free energy of activation ($\Delta G^\ddagger$), the self-accelerating decomposition temperature (T_{SADT}) and the critical temperature of thermal explosion (T_b) are $59.42 \text{ J mol}^{-1} \text{ K}^{-1}$, $169.5 \text{ kJ mol}^{-1}$, $1141.26 \text{ kJ mol}^{-1}$, 457.3 K and 468.1 K , respectively.

© 2014 Feng-Qi Zhao. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

1. Introduction

Combustion catalysts as ballistic modifiers are important ingredients in solid rocket composition [1–3]. The function of combustion catalysts is to adjust the burning rate and to reduce the pressure exponent of solid propellants. Metal oxides such as ferric oxide and copper chromite are highly effective ballistic modifiers, but they impose a penalty on the energetic of propellant system due to their inert nature. Energetic combustion catalysts [4–6] are envisaged to achieve the catalytic effect on burning rate without much adverse effect on the energetic of the solid rocket propellants. Therefore, energetic combustion catalysts are preferable over the inert combustion catalysts in solid propellants.

4-Amino-3,5-dinitro-1H-pyrazole (LLM-116) [7–9] was synthesized initially in 2001. It was a small molecule compound with high energy (the detonation velocity is 9008 m/s) and low mechanical sensitivity (the friction sensitivity is 0%), but the acidity of LLM-116 limits its application in solid rocket composition. So some researchers found that it can be used as a key intermediate for the production of trinitropyrazole [10,11] and some energetic salts [12,13]. The copper salt of 4-amino-3,5-dinitropyrazole ($[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$) was designed and synthesized as a new high energy catalyst, which will be used as an energetic combustion catalyst to

adjust the burning properties of solid propellant. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is the key energetic material and the most common oxidizer in the solid rocket propellant. Nitrocellulose (NC) is the most commonly used binder in solid rocket propellant. Considering the limited loading of RDX and NC in the rocket, it is crucial to further improve its decomposition efficiency to maximize the energy production and to decrease its burning temperature for easy operation and control. So, the catalysis of RDX and NC thermal decomposition is very important. The studies of the structure, the thermal behaviors and catalytic activity are a very important starting point for the selection, application and exploitation of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$. To the best of our knowledge, these studies have not been reported previously.

The aim of this work is to use the acidity of LLM-116 to synthesize 4-amino-3,5-dinitropyrazole copper salt (Scheme 1), obtain the single crystal of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$ using water as solvent, study the non-isothermal decomposition kinetics of ($[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$) under static state by means of different heating rate differential scanning calorimetry (DSC) [14–18], and examine the catalytic activity on RDX and NC.

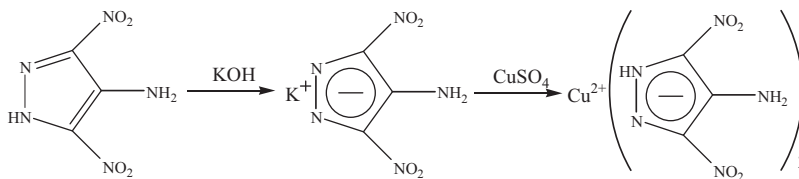
2. Experimental

2.1. Materials

4-Amino-3,5-dinitropyrazole was synthesized according to the procedures reported in Ref. [9].

* Corresponding author.

E-mail address: npecc@163.com (F.-Q. Zhao).

Scheme 1. Synthetic route of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$.

2.2. Synthesis

2.2.1. Synthesis of 4-amino-3,5-dinitropyrazole potassium salt (ADNPK) [13]

4-Amino-3,5-dinitropyrazole (1.78 g, 0.01 mol) was suspended in 20 mL of H_2O then KOH (0.56 g, 0.01 mol) in 10 mL H_2O was added. The reaction mixture was stirred at 60°C for 1 h, 40 mL of methanol was added, and the resulting mixture was slowly cooled to 0°C . Some brown sediments of ADNPK formed and were filtered, washed with methanol and dried under vacuum to give the product (1.82 g, 86.26%).

IR (KBr, cm^{-1}): ν 1570, 1372 ($-\text{NO}_2$), 3446, 3341, 950 ($-\text{NH}_2$), 1638, 1441, 829, 750 (Pyrazol).

Anal. calcd. for $\text{C}_3\text{H}_4\text{N}_5\text{O}_5 \text{ K}$ (%): C 15.72, H 1.747, N 30.57, K 17.03; found: C 15.69, H 1.740, N 30.09, K 17.10.

2.2.2. Synthesis of 4-amino-3,5-dinitropyrazole copper salt ($[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$)

ADNPK (2.13 g, 0.01 mol) was suspended in 20 mL of water, then CuSO_4 (1.25 g, 0.005 mol) in 10 mL H_2O was added. The reaction mixture was stirred at 80°C for 2 h. The resulting solids were filtered and dried in air to give the product obtained (1.91 g, 93.6%).

IR (KBr, cm^{-1}): ν 1573, 1378 ($-\text{NO}_2$), 3446, 3340, 952 ($-\text{NH}_2$), 1638, 1441, 829, 751 (Pyrazol).

Anal. calcd. For $\text{C}_6\text{H}_4\text{N}_{10}\text{O}_8\text{Cu}$ (%): C 16.22, H 2.252, N 31.53, Cu 14.41; found: C 16.21, H 2.254, N 31.49, Cu 14.38.

2.3. Determination of the single crystal structure

Single crystals suitable for X-ray measurement were obtained by slow evaporation of an aqueous solution of the titled compound at room temperature. Diffraction data were collected on a Bruker SMART diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.071073 \text{ nm}$) in φ and ω scan modes at 296 K. Absorption corrections were applied using the SADABS program. The structures were solved by the direct methods and successive Fourier difference syntheses (SHELXTL-97), anisotropic thermal parameters for all non-hydrogen atoms were refined by the full-matrix-block least-squares method on F^2 (SHELXTL-97) [19]. Hydrogen atoms were added according to the theoretical models. Crystal data, experimental details and refinement results were summarized in Table S1 (Supporting information).

2.4. Thermal experimental instruments and conditions

DSC measurements were carried out on a Model TA-910 USA instruments. The operation conditions were as follows: heating rates, 5 K min^{-1} , 10 K min^{-1} , 15 K min^{-1} and 20 K min^{-1} ; sample mass, 0.5–1 mg; aluminum sample cell; atmosphere, static nitrogen at 0.1 MPa.

2.5. Catalytic activity test

The obtained $\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2$ was mixed with RDX in 1:5 (wt.%) and NC in 1:5 (wt.%) respectively and the two mixed samples were used for the DSC experiment. The experiment was

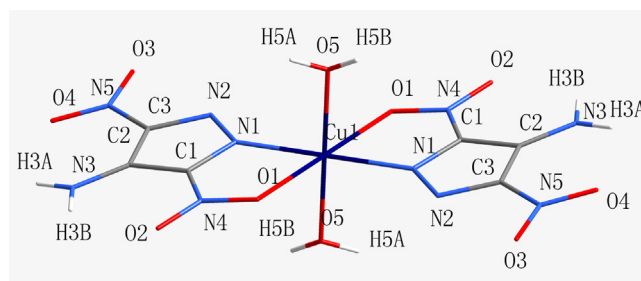
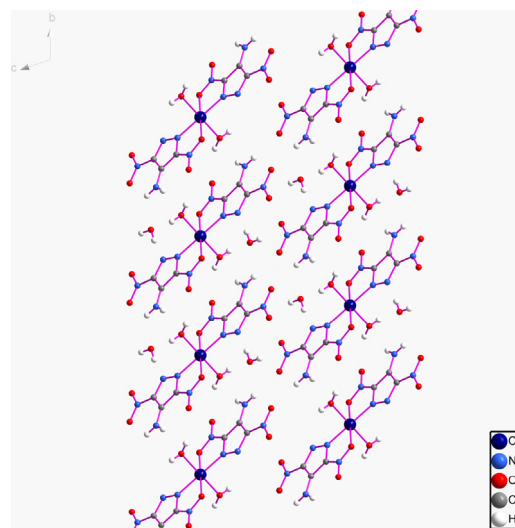
performed at a programmed heating rate of 10 K min^{-1} (sample mass, 0.5–1 mg; aluminum sample cell; atmosphere, static nitrogen at 0.1 MPa).

3. Results and discussion

3.1. Crystal structure

Molecular structure of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$ was illustrated in Figs. 1 and 2. Selected bond lengths and bond angles of the titled compound are summarized in Tables S2 (Supporting information).

The analytical results indicate that $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$ crystallizes in triclinic with $P\bar{1}$ space group. The molecule of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$ contains a copper cation, an organic ligand LLM-116 anion, and two crystal water (Fig. 1). Each copper ion is bonded with four ligands, and the coordination number of copper ion is 6. Two ligands are bidentate ligands and the other two ligands are two crystal water. The bidentate ligand is connected to the copper ion by different coordinating atoms, one of which is the oxygen atom in the nitro group and the other is the nitrogen atom in pyrazole ring.

Fig. 1. The coordination environments of Cu atoms in $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$.Fig. 2. The packing molecules of $[\text{Cu}(\text{adnp})_2(\text{H}_2\text{O})_2]$.

Download English Version:

<https://daneshyari.com/en/article/1254872>

Download Persian Version:

<https://daneshyari.com/article/1254872>

[Daneshyari.com](https://daneshyari.com)