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Crystal structure and explosive performance of a new CL-20/caprolactam cocrystal ☆

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HIGHLIGHTS

- A novel CL-20/caprolactam cocrystal has been designed and characterized.
- The crystal structure, mechanism and performance are characterized and discussed.
- The formations of cocrystal mainly rely on strong hydrogen bonds interactions.
- The two cocrystal formers can be separated to obtain β-CL-20.
- Provide a good guide for the design of future CL-20 and other explosive cocrystals.

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ABSTRACT

Co-crystallization is an effective way to improve performance of the high explosive 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20). A new CL-20/caprolactam (CPL) cocrystal has been prepared by a rapid solvent evaporation method, and the crystal structure investigations show that the cocrystal is formed by strong intermolecular hydrogen bond interaction. The cocrystal can only be prepared with low moisture content of the air, because water in the air has a profound effect on the cocrystal formation, and it can lead to crystal form conversion of CL-20, but not the formation of cocrystal. The CL20/CPL explosive possess very low sensitivity, and may be used as additive in explosives formulation to desensitize other high explosives.

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1. Introduction

Energetic materials (explosives, propellants and pyrotechnics) are used extensively for both civilian and military applications. There are ongoing research programs worldwide to develop new explosives and propellants with higher explosive performance and enhanced insensitivity to thermal or mechanical shock [1]. In recent years, how to improve the explosive performance of existing energetic materials have received a great amount of interest [2–5]. For this purpose, a better approach is to introduce co-crystallization techniques to obtain explosives with excellent comprehensive performance.

Co-crystallization is an effective method to improve the physical and chemical properties of crystalline solid, and it has been widely used in the field of pharmaceutical science [6–8]. By co-crystallization technology, the rate of dissolution, thermal stability and biological activity of the drug can be effectively improved without changing the structure of pharmaceutical active ingredient (API) [9–12]. Currently, researchers also apply this technology to the field of energetic materials as an effective means of changing the density, melting point, decomposition temperature and sensitivity of the explosives. For example, 17 cocrystals of TNT with a range of aromatic or heterocyclic co-formers by Landenberger and Matzger revealed an alteration of key properties including density, melting point and decomposition temperature compared with TNT [13]. Recently, the cocrystals of HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) with a wide variety of co-formers have been reported, which also afford a tremendous reduction in sensitivity compared to pure HMX [14]. Such cases suggest that it is helpful to applied co-crystallization techniques to modulate the physical and chemical properties of existing explosives.

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CL-20, also called HNIW, is a nitroamine explosive with the formula $C_6H_6N_{12}O_{12}$, primarily used in propellants. It has better oxidizer-to-fuel ratio than the conventional high explosives HMX and RDX [15,16]. However, the high sensitivity usually restricts the storage, transportation, and widely application of CL-20 explosive. In order to improve its safety, a good method is to co-crystallize CL-20 with other insensitive explosive or non-explosive substances to form a new crystal structure [17,18]. Not long ago, Bolton and co-workers prepared a cocrystal of TNT and CL-20, which improves the security of CL-20 while barely reduce the energy [19]. In addition, its density, decomposition temperature and so on have also been modified. In 2012, Bolton et al. reported that a cocrystal of CL-20 and HMX had similar safety properties to HMX, but firing power closer to CL-20 [20]. Although several cocrystals have now been designed to improve the explosive performance of CL-20, the cocrystals is usually difficult to be obtained because of the lack of strong predictable interactions in the chemical structures of its components. The investigation of new CL-20 cocrystal can help to study the formation mechanism and subsequent crystal design and preparation. In addition, the CL-20 cocrystal with non-explosives is needed to obtain explosives with low energy output, which can be used to meet some special requirements, such as smooth blasting, pre-splitting blasting and controlled blasting engineering. In this paper, the non-explosive CPL was chosen to form cocrystal with CL-20, and the cocrystal has been prepared and crystal structure as well as explosive performance are characterized and discussed, which will provide a good guide for the design of future cocrystals of CL-20 and other explosive.

2. Experimental

2.1. Materials

ε-CL-20 was supplied by the Beijing Institute of Technology. Analytical grade caprolactam and anhydrous acetone were provided by Chengdu Institute of Chemical Reagents.

2.2. Cocrystal preparation

Crystallization experiments was conducted by dissolving a molar ratio of 1:5 mixture of ε-CL-20 (4.44 mg) and CPL (5.65 mg) in a minimum amount of anhydrous acetone (dried in the 4A molecular sieve). The solvent was evaporated at 40 °C over a period of several minutes, and a new energetic cocrystal of CL-20/CPL was formed.

2.3. Optical microscopy

Optical micrographs of the crystals were taken under the SK2005A polarization microscope.

2.4. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance with a Cu Kα radiation (λ = 1.54439 Å), the voltage and current applied were 40 kV and 40 mA, respectively. The data were collected over an angle range from 5° to 50° with a scanning speed of 0.02° per second [21].

2.5. Single crystal X-ray diffraction

The single-crystal X-ray diffraction data of the cocrystal was collected on an Xcalibur, Eos diffractometer. The crystal was kept at 293.15 K during data collection. Crystal structures was solved by direct method using SHELXS, structure solution program using direct method and refined with the SHELXL, refinement package using Least Squares minimisation [22].

2.6. Differential Scanning Calorimeter (DSC)

DSC was performed on a NETZSCH STA 449C Differential Scanning Calorimeter. 1.45–1.78 Mg of samples were placed in aluminium pans and the thermal behaviour of the samples were studied under nitrogen (30.0 ml/min) purge at a heating rate of 10 °C/min over a range from 50 °C to 300 °C [23].

2.7. Infrared spectroscopy (IR)

IR absorption spectra were obtained at a resolution of 4 cm^{-1} using a Nicolet 6700 infrared spectrometer, with each spectrum obtained as the average of 25 individual spectra. Each spectrum was scanned in the range of 400–4000 cm^{-1} with a minimum of six scans [24].

2.8. The drop height at which 50% initiation occurred (H_{50}) and friction sensitivity

The H_{50}: It is based on the varying of the impact energy value in each trial. Depending on the result of previous, the level of impact energy is decreased after ignition for the next trial and increased after "no reaction". In this study we used a 5 kg drop weight, after 25 trials, the level of impact energy with 50% probability of ignition and its standard deviation is determined statistically [25].

The friction sensitivity: The determination of the friction sensitivity was performed referring to the method of WJ1870289 standard and WJ1871280 standard [26]. Dose is 20 mg, pendulum quality is 5 kg, the swing angle is 70° and gauge pressure is 23 MPa.

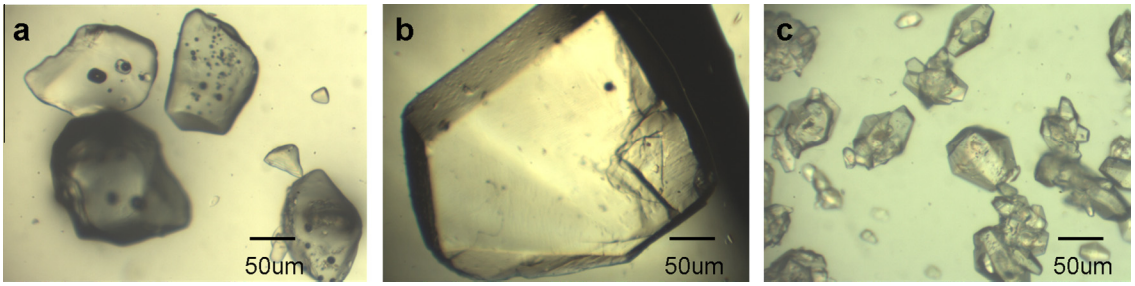

Fig. 1. Microscope images of CPL (a), CL-20/CPL cocrystal (b) and ε-CL-20 (c).

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