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Cocrystal explosive hydrate of a powerful explosive, HNIW, with enhancing safety

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ABSTRACT:

A novel cocrystal explosive hydrate containing HNIW (hexanitrohexaazaisowurtzitane), NMP (N-methyl-2-pyrrolidone) and water was synthesized through cocrystallization. The crystal structure was characterized by power x-ray diffraction (PXRD) and single crystal x-ray diffraction (SXRD). This crystalline belongs to the monoclinic crystal system with space group P2(1)/c. The properties of cocrystal hydrate including thermal behavior, impact sensitivity and detonation performance were also evaluated. The cocrystal hydrate shows a unique thermal behavior with an endothermic peak and a decomposition peak at 91 and 252 ℃，respectively. Besides, the cocrystal hydrate displays an impact height with 50% ignition probability of 112 cm, indicating a substantial reduction in impact sensitivity compared to pure α-HNIW and ε-HNIW. Furthermore, although the power is diluted, the cocrystal hydrate is predicted to have more excellent detonation performances than pure DNAN (2,4-dinitroanisole) and TNT (trinitrotoluene). Therefore, the cocrystal hydrate may be a promising low sensitivity explosive.

Keywords: Cocrystal explosive; HNIW; NMP; safety; Property.

Abbreviations: hexanitrohexaazaisowurtzitane (HNIW or CL-20); N-methyl-2-pyrrolidone (NMP); 2,4-dinitroanisole (DNAN); cyclotetramethylenetetranitramine (HMX); cyclotrimethylenetrinitramine (RDX); trinitrotriaminobene (TATB); nitrotriazolone (NTO); diaminodinitroethene (FOX-7); benzotrifuroxan (BTF); trinitrotoluene (TNT); dinitrobenzene

(DNB); ammonium nitrate (AN); benzo-18-crown-6 (B18C6).

1. Introduction

Energetic materials such as explosive, propellants and pyrotechnics are a class of chemical substances generally containing nitro, amino and azide groups in molecules, which release a large amount of potential energy accompanied with high temperature and high pressure through a rapid decomposition[1,2]. Energetic materials are thus widely used in military and civil fields for a long time, such as HNIW (hexanitrohexaazaisowurtzitane), HMX (cyclotetramethylenetetranitramine) and RDX (cyclotrimethylenetrinitramine) are applied in bombs, shells and warheads due to their high explosive performances. Contrarily, TATB (trinitrotriaminobene), NTO (nitrotriazolone) and Fox-7 (diaminodinitroethene) are used as explosives filling for insensitive ammunitions owing to their excellent safety. However, there is an obvious feature that performance runs parallel to sensitivity among existing explosives, failing to meet the requirements of insensitive high energy explosives for modern weapon applications[3]. Therefore, researchers all over the world in energetic material fields have taken extensive studies on development of novel energetic materials that have excellent performances with reduced sensitivity to external stimuli such as impact, friction and shock wave.

To reduce sensitivity while maintaining high performance, one strategy is to synthesize new insensitive high power energetic materials, but which is a complex and time-consuming process[4-6]. Fortunately, another intriguing strategy is to utilize the cocrystallization methodology to achieve explosive cocrystals, integrating both an explosive and a coformer into one crystal structure by intermolecular interactions such as hydrogen bonds, π-stacking, or van der waals forces[7,8]. Currently, cocrystals are emerging as a promising method to synthesize enhanced energetic

materials as well as tune properties of energetic materials owing to the alterations of components and structures for explosives in energetic material fields. However, reports on the cocrystallization of energetic materials are very scarce from open literatures so far, whereas several studies indicated that apart from offering potential improvements in density, melting point and decomposition temperature, cocrystal explosives can enhance other key properties of the existing explosives including sensitivity, detonation velocity and detonation pressure. For example, the impact sensitivity of HNIW, HMX and BTF (benzotrifuroxan) were large reduced by cocrystallizing with some aromatic explosives and some non-energetic compounds [9-14]. Therefore, explosive cocrystals open an effective strategy to improve properties of energetic materials and attract increasing attention in energetic science at present. Nowadays, to our knowledge, the reported explosive cocrystals only contain two components, but in terms of the power to modify properties, it may be concluded that mult-component cocrystals will produce a much wider range of alternations in properties to achieve energetic materials with further improved performance.

HNIW (commonly referred to CL-20, Fig.1) has four known different polymorphs, α, β, γ, and ε, with ambient conditions α-HNIW containing water molecule (HNIW-H_2O) and ε-HNIW having highest density ($2.04 g/cm^3$)[15]. HNIW is considered one of the most powerful explosive, possessing higher oxygen balance, density and energy. However, it is too sensitive to mechanical stimuli (impact or friction) and shock wave to meet the stringent safety requirements for modern weapons, consequently hampering its further applications[16-17]. NMP (N-methyl-2-pyrrolidone, Fig.1) represents one of the most unique functional groups in crystal engineering, featuring a carbonyl group, in spite of it belonging to a nonenergetic material[18]. Additionally, the O atom in carbonyl groups and water molecules is one of the stronger hydrogen bond acceptor, which readily

forms a hydrogen bond with a weak donor. Therefore, cocrystallizing them together may help us to further reduce the sensitivity of HNIW. Besides, explosive molecules commonly possess nearly saturated with nitro groups, which give very few predictable interactions and synthons for designing cocrystals among energetic materials. Fortunately, Matzger and Millar research groups analyzed the intermolecular interactions of the structures of cocrystals, offering some insights into designing energetic cocrystals[10, 19-21]. In comparison with similar cocrystals reported by Millar, we present a novel ternary cocrystal of HNIW and characterize its properties in detail. Our study will further contribute to the rational design of HNIW cocrystals and the exploitation for multi-component cocrystals, which may promote the development and application of cocrystals in energetic materials.
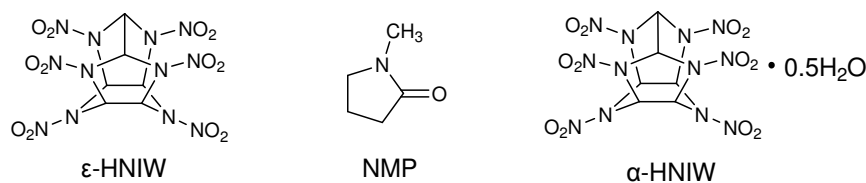
Fig. 1 Molecular structure of ε-HNIW (left), NMP (middle) and α-HNIW (right)

In this work, a novel 1:2:1 HNIW/NMP/H_2O cocrystal explosive hydrate was discovered and synthesized by cocrystallizing from slow evaporation solvent. The crystal structure of the cocrystal explosive hydrate was determined by single crystal x-ray diffraction (SXRD). Additionally, we also study properties of the cocrystal explosive hydrate including thermolysis, sensitivity and detonation performance in detail.

2. Experimental section

2.1 Materials

ε-HNIW and α-HNIW were supplied by Liaoning Qingyang Chemical Industry Co., Ltd. NMP was obtained from Mianyang Rongsheng Chemical Industry Co., Ltd. Solvents and other

reagents were purchased from trade and used as received.

2.2 Synthesis of the HNIW/NMP/H2O cocrystal explosive hydrate

ε-HNIW (438 mg, 1 mmol) was added to a mixture of 2 ml of NMP and 0.5 ml of water, mildly heated to all ε-HNIW dissolution. The solution was allowed to evaporate slowly at room temperature over several days. The colorless cocrystal hydrates were precipitated, filtered and dried under ambient conditions.

2.3 Morphology characterization

The morphologies of cocrystal hydrates, α-HNIW and ε-HNIW were carried out by a Zeiss axio scope A1 microscope.

2.4 Power X-ray diffraction (PXRD)

XRD data were collected on a Bruker D8 Advance diffractometer using Cu-Kα radiation (λ=1.54056 Å) at 35 kV and 40 mA. The samples were scanned within the scan range of 2θ=7.5° to 45° continuous san with a step size of 0.015° and a scan speed of 0.2 s per step. Moreover, the PXRD pattern of the cocrystal hydrate was simulated by its CIF file and Reflex Module in Materials Studio package with the same sets as experiment[22].

2.5 Single crystal X-ray diffraction (SXRD)

Single crystal of suitable quality was chosen and purged with a cooled nitrogen gas stream at 293 K throughout the data collection. X-ray reflections were collected on a Xcalibur Eos CCD detector with graphite-monochromated Mo− Kα radiation (λ=0.71073 Å). Data were collected and processed using Olex2 software. Structure was solved by direct methods and SHELX was used for structure solution and least-squares refinement[23].

2.6 Thermal analysis

Differential Scanning Calorimetery (DSC) was performed on a TA Q100 instrument. 1-2 mg of cocrystal hydrate was heated from 25 to 350 ℃ at a heating rate of 10 ℃/min under nitrogen (50 ml/min) atmosphere.

Thermogravimetry (TG) test was recorded on a TA Q600 instrument by heating about 2 mg of cocrystal hydrate at a rate of 10 ℃/min under nitrogen (50 ml/min) atmosphere.

Hot-stage Optical Microscopy (HSM) was examined using a Caikon CK-3000 hot stage and a HIROX-1300 optical microscope. The heating rate was 5 ℃/min.

2.7 Impact sensitivity

The impact sensitivity was performed with a WL-1 type impact sensitivity instrument according to GJB-772A-97 standard method 601.2[24]. The experimental conditions were: drop weight, 2 kg; sample mass, 30 mg. The impact sensitivity of test sample was expressed by the drop height of 50% explosion probability (H_{50}).

2.8 Detonation performance Prediction

The detonation performances of the cocrystal hydrate, ε-HNIW , α-HNIW and DNAN were evaluated by the linear output thermodynamic user-friendly software code[25].

3. Results and discussion

3.1 Morphologies

The optical microscopy images for the cocrystal hydrate, ε-HNIW and α-HNIW are shown in Fig. 2. The observed crystal morphologies of them are distinctly different. The cocrystal hydrates exhibit colorless prism type crystal morphology with smooth and integrated surfaces, whereas the α-HNIW and ε-HNIW present a block type microstructure and a spindle-like shape, respectively. These differences in crystal morphologies can be attributed to their different microscopic

6

structures, suggesting a new structure formation. Additionally, an average particle size of the

cocrystal hydrate is about 400 μm，which is cleare larger than that of α-HNIW and ε-HNIW.

Therefore, cocrystallization provides a potential methodology to control morphologies and sizes of

explosive crystals.

**Fig. 2** Optical microscopy images of α-HNIW (a), cocrystal hydrate (b), and ε-HNIW (c)

3.2 Solid-state characterization

As shown in Fig. 3, cocrystal hydrate has a unique powder X-ray diffraction (PXRD) pattern

that differs from those of α-HNIW and ε-HNIW. In particular, a series of new strong peaks occur

in the PXRD curve of cocrystal hydrate, whereas no corresponding peaks appear in the PXRD

patterns of α-HNIW and ε-HNIW. Furthermore, the differences in PXRD curves among them,

further indicate that the cocrystal hydrate is a new crystalline form rather than a phase

transformation of HNIW polymorphs. Moreover, as presented in Fig. 3, the experimental and

simulated PXRD profiles of the cocrystal hydrate match with each other. Additionally, the

cocrystal exhibits a pattern due to preferred orientation, as it exhibits in a shape of block prism

shown in Fig. 2.
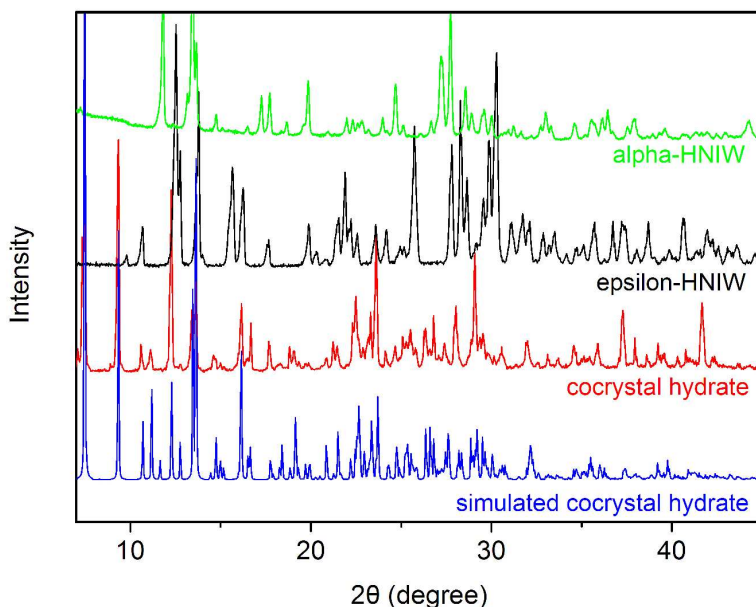
Fig. 3 PXRD patterns of cocrystal hydrate, α-HNIW and ε-HNIW

3.3 Structure of the cocrystal hydrate

Single crystal X-ray diffraction (SXRD) analysis of HNIW/NMP/H2O (1:2:1) cocrystal shows that they crystallize in the monoclinic system with space group P2(1)/c. The asymmetric unit consists of two molecules of NMP and one molecule each of HNIW and Water. In the cocystal, the skeleton is made of HNIW and NMP. As shown in Fig. 4, the two components represent good layer structure, which are connected by mid-strength hydrogen bonds. The hydrogen bonds involve the interactions of nitro-O···alky-H (2.28-2.68 Å) and carbonyl-O···alky-H (2.34-2.56 Å). Moreover, the two components compose the larger cavities, in which the water molecules are located. Actually, water molecules play an important role in the cocrystal formation, such that they interact with all other components of the asymmetric unit. Via one water molecule, four new hydrogen bonds form to make crystal more stable, in which the hydrogen bonds between O-H···O=C are stronger with 1.95-2.21 Å, while hydrogen bonds of

O···HC are weaker with 2.40-2.64 Å.
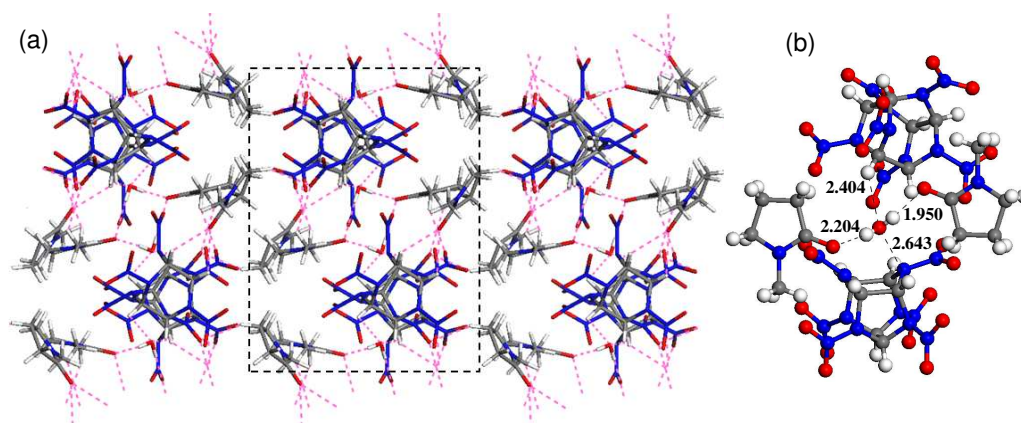
Fig. 4 Crystal structure of the cocrystal hydrate: (a) structure of the super cell; (b) typical intermolecular interactions in the super cell unit

3.4 Thermal analysis

The thermal behavior of cocrystal hydrate was investigated by DSC and TG analyses. A smaller endotherm between 80 to 105 ℃ (Fig. 5), can be attributed to the melting of the cocrystal hydrate accompanying water release, whereas which is not present in α-HNIW and ε-HNIW. A unique endothermic peak occurs at 91 ℃, which is significantly higher 115 ℃ than the melting point of NMP (M.P.= -24 ℃[26]). Besides, the DSC trace of cocrystal hydrate shows a strong exothermic peak at 252 ℃, which corresponds to the decomposition event of cocrystal hydrate, slightly higher than those of α-HNIW (T_{max}=245 ℃[27]) and ε-HNIW (T_{max}=249 ℃[27]). In addition, the cocrystal hydrate displays two weight loss steps in TG curve (Fig. 5), suggesting heterogeneous decomposition process. A stable weight loss starts at 80 ℃, due to the evaporation of H_2O and NMP, followed by the weak decomposition of NMP. Another rapid weight loss appears in the temperature range of 220-255 ℃, mainly attributed to the intense thermal decomposition of HNIW. Furthermore, the thermal behavior of crystal hydrate was assessed by HSM (Fig. 6). Water release and partial melting of cocrystal hydrate was observed between 82 to

91 ℃. The crystal converts to liquids with temperature increasing. In short, compared with the melting point or decomposition temperature of α-HNIW, ε-HNIW and NMP, cocrystal hydrate exhibits a new distinct thermal behavior, due to incorporating NMP into α-HNIW through cocrystallization, implying that multi-component cocrystal may generate a wider range alteration in properties of energetic materials.
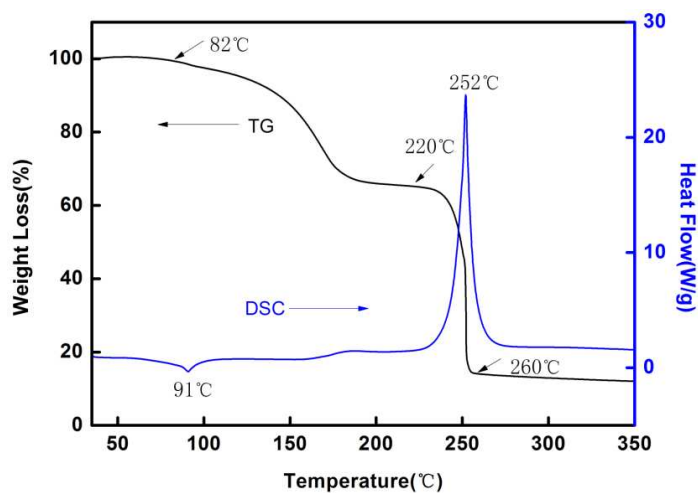
Fig. 5 DSC and TG curves of cocrystal hydrate
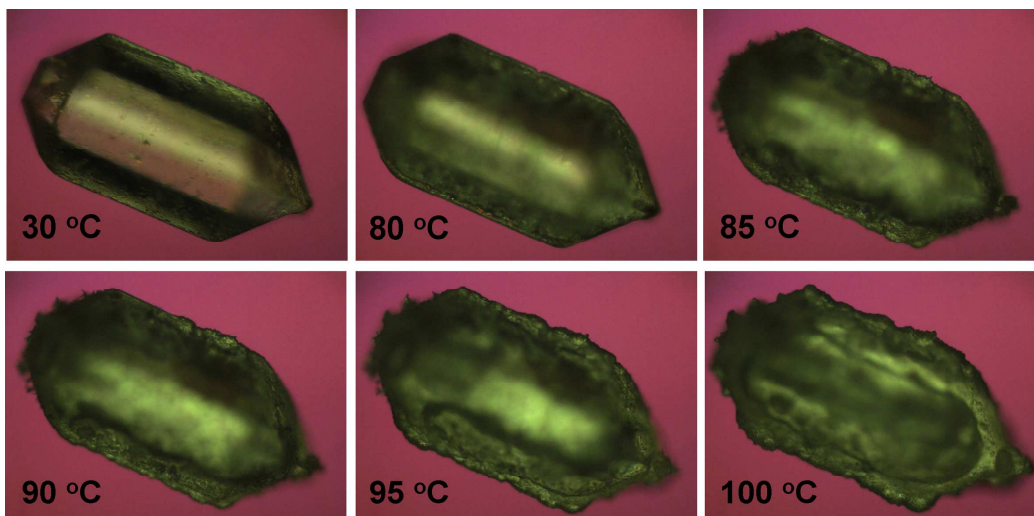
Fig. 6 HSM images of cocrystal hydrate

3.5 Sensitivity

Sensitivity is one of the most important properties of energetic materials that affect their

developments and applications. Sensitivity of energetic materials to different stimuli (such as impact, friction and shock) is often used to assess their safeties. The cocrystal hydrate, α-HNIW and ε-HNIW were subjected to impact sensitivity test. The results were expressed by the drop height of 50% explosion (H_{50}) and tabulated in Table 1. The H_{50} values for α-HNIW and ε-HNIW is 16 and 14 cm, respectively, but the cocrystal hydrate displays H_{50} of 112 cm. Additionally, the drop height for cocrystal hydrate is about seven times higher than that of pure α-HNIW, suggesting a remarkable reduction in impact sensitivity relative to pure α-HNIW and ε-HNIW. This observation further indicated that mult-component cocrystal offers a potential methodology to tune the sensitivity of explosives.

Table 1 Results of impact sensitivity

Samples	Impact sensitivity (H_{50}, cm)
ε-HNIW	14
α-HNIW	16
Cocrystal hydrate	112

The reasons accounted for the decreased sensitivity of the cocrystal hydrate are mainly the results of the incorporation of the non-energetic coformers into HNIW through cocrystallization . Besides, enhanced hydrogen bonds formed in cocrystal hydrate may act as an energy pathway to dissipate heat effectively for hindering formation of hot spots and . Thereby, this decreases the probability of initiation via hot spots, leading to a decrease in sensitivity[28].

3.6 Detonation performance prediction

Detonation performances including detonation velocity and detonation pressure are another critical property to evaluate the energy of explosives. Although the power of cocrystal hydrate is diluted via cocrystallization with nonenergetic materials. Both the detonation velocity and detonation pressure of cocrystal hydrate are predicted to be 7098 m/s and 21.2GPa, respectively,

which are less than those of pure α-HNIW and pure ε-HNIW (Table 2). It may be explained by the fact that cocrystal hydrate has lower density and lower oxygen balance compared with α-HNIW and ε-HNIW. However, the cocrystal hydrate is potentially useful, which may be used as a novel low sensitive explosive due to higher safety and higher power relative to DNAN and TNT.

Table 2 Results of detonation performance prediction

Samples	Density(g/m^3)^a	Detonation performance	
		Detonation velocity (m/s)	Detonation pressure (GPa)
ε-HNIW	2.035	9385	44.9
α-HNIW	1.952	9378	43.4
DNAN	1.341	5706	11.9
TNT	1.654	6650	19.1
Cocrystal hydrate	1.602	7098	21.2

^{a}Crystallographic density at room temperature

4. Conclusions

A novel cocrystal explosive hydrate (three component cocrystal) composed of HNIW, NMP and water in a 1:2:1 molar ratio was synthesized and characterized. This cocrystal hydrate is mainly stacked through OH···O and CH···O hydrogen bonds, offering further insight into designing HNIW cocrystals. The cocrystal hydrate displays a unique thermal behavior with an entire melting and a decomposition peak at 100 and 252 ℃, respectively. Moreover, the cocrystal hydrate exhibits significantly reduced impact sensitivity compared with α-HNIW and ε-HNIW and more excellent predicted detonation performances relative to pure DNAN and TNT. Therefore, the cocrystal hydrate may be used as a promising low sensitive explosive. In summary, cocrystal methodology offers an effective strategy to achieve energetic materials with improved performances.

Acknowledgements

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