A novel energetic cocrystal composed of CL-20 and 1-methyl-2,4,5-trinitroimidazole with high energy and low sensitivity

Pengbao Lian, a Luyao Zhang, b Hongping Su, b Jun Chen, c Lizhen Chen a and Jianlong Wang a*

a School of Chemical Engineering and Technology, North University of China, College Road 3, Taiyuan, Shanxi 030051, People’s Republic of China; b Scientific Research and Technology Development Department, Gansu Yin’guang Chemical Industry Group, Baiyin, Gansu 730900, People’s Republic of China; and c Hubei Dongfang Chemical Industry Co., Ltd, Xiangyang, Hubei 441403, People’s Republic of China. *Correspondence e-mail: wangjianlong@nuc.edu.cn

A cocrystal explosive comprising 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and 1-methyl-2,4,5-trinitroimidazole (MTNI) (molar ratio, 1:1) was synthesized. The structure of the cocrystal was characterized by single-crystal X-ray diffractometry. Its structure was further determined by powder X-ray diffraction, infrared spectroscopy and differential scanning calorimetry which showed that its morphology was different from the morphology of the mechanical mixture of two raw materials. The decomposition temperature of the cocrystal is lower than that of CL-20 and MTNI. The calculated detonation performance is slightly lower than that of HMX, but the cocrystal has excellent sensitivity performance relative to that of CL-20, even lower than that of RDX. These features make this cocrystal ideal to be used in applications with low-sensitivity requirements.

1. Introduction

Energetic materials are widely used in the civil and military sectors, such as mining, oil industry, missiles, torpedoes, etc. (Zhang & Shreeve, 2014; He & Shreeve, 2015; Fischer et al., 2014). CL-20 has high detonation performance, which is currently one of the best high energetic materials in application (Simpson et al., 1997; Geetha et al., 2003; Mandal et al., 2009; Urbelis & Swift, 2014; Dong et al., 2014). CL-20 has four crystal types: α, β, γ and ε, among which ε-CL-20 is suitable for industrial applications due to the highest density and the highest detonation performance. However, the application fields of ε-CL-20 is limited due to its high sensitivity (Nair et al., 2005; Yu et al., 2013; Shen et al., 2014; Nedelko et al., 2000).

Technologies involving coating (Hoffman, 2000; Heijden & Bouma, 2004; Yu et al., 2013; Yang et al., 2015), nano (Bayat & Zeynali, 2011; Doblas et al., 2016; Song et al., 2018; Qiu et al., 2015; An et al., 2017; Gao et al., 2014), recrystallization (Heijden & Bouma, 2004) and cocrystallization (Yang et al., 2013; Guo et al., 2015; Bolton & Matzger, 2011; Liu, An et al., 2018; Guo et al., 2013; Liu et al., 2016; Gao et al., 2014; Bolton et al., 2012; Xue et al., 2017; Anderson et al., 2014; Doblas et al., 2016; Ghosh et al., 2018; Sun et al., 2018, 2019; Tan et al., 2019; Bennion et al., 2016; Yang et al., 2018; Zhang et al., 2018; Xu et al., 2015; Ma et al., 2017; Tang et al., 2020; Anderson et al., 2016; Gao, Jiang et al., 2017; Liu, Yan et al., 2019; Liu, Duan et al., 2018; Yang et al., 2012; Millar et al., 2012; Wang et al., 2014; Sinditskii et al., 2016; Gao, Du et al., 2017; Liu, Duan et al., 2019; Fei et al., 2019; Liu, Lv et al., 2019; Xue et al., 2020) have
been used to reduce the sensitivity of ε-CL-20. In recent years, cocrystallization technology was an important means to reduce the sensitivity of energetic materials. The hydrogen bonds and π–π stacking interactions in different molecules were used to synthesize cocrystals (Lara-Ochoa & Espinosa-Pérez, 2007; Bond, 2007). Recently, scientists have reported a good many examples of CL-20-containing cocrystals, such as CL-20/2,4,6-trinitrotoluene (Doblas et al., 2016; Yang et al., 2013; Guo et al., 2015; Bolton & Matzger, 2011; Liu, An et al., 2018), CL-20/tetrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (Ghosh et al., 2018; Doblas et al., 2016; Gao et al., 2014; Bolton et al., 2012; Xue et al., 2017; Anderson et al., 2014; Sun et al., 2018), CL-20/hydrogen peroxide (Bennion et al., 2016), CL-20/2,4-dinitro-1-methylimidazole and CL-20/4,5-dinitro-1-methylimidazole (Yang et al., 2018), CL-20/1,3,5-triamino-2,4,6-trinitrobenzene (Xu et al., 2015), CL-20/1-methyl-3,4,5-trinitropyrazole (Tang et al., 2020; Ma et al., 2017), CL-20/hexahydro-1,3,5-trinitro-1,3,5-triazine (Gao, Jiang et al., 2017) and CL-20/2,4-dinitroimidazole (2,4-DNI) (Liu, Yan et al., 2019). The detonation velocity, detonation pressure and impact sensitivity of CL-20/H₂O₂ cocrystal (orthorhombic) were 9606 m s⁻¹ and 47.00 GPa, respectively, which were higher than ε-CL-20; meanwhile, its impact sensitivity was 24 cm (H₉₀) just below that of ε-CL-20 (29 cm) (Bennion et al., 2016). The energetic performance of other CL-20-containing cocrystals was lower than ε-CL-20, but their sensitivity was better than ε-CL-20.

Judging from the data in the existing literature, CL-20-containing cocrystals have not achieved higher energy density and lower sensitivity. Therefore, the current research into CL-20-containing cocrystals aims to minimize reduction of energy density and minimize the increase in sensitivity (Xue et al., 2020; Fei et al., 2019; Liu, Duan et al., 2019; Liu, Lv et al., 2019; Sun et al., 2019; Gao, Du et al., 2017; Sinditskii et al., 2016).

Hence, a cocrystal compound of CL-20 and MTNI (see Scheme 1) was synthesized by slowly concentrating by evaporation its organic solution at room temperature and with a 1:1 molar ratio. As a replacement candidate for TNT, MTNI has a moderate density (1.78 g cm⁻³), which is higher than that of TNT (1.65 g cm⁻³), while a relatively high detonation velocity (8768 m s⁻¹), a relatively high detonation pressure (33.74 GPa), low impact sensitivity (11 J) and low friction sensitivity (> 360 N) have been calculated or measured (Lian et al., 2022). Therefore, MTNI may be an attractive partner (which has high detonation performance and low sensitivity) for CL-20 in the formation of a high energetic cocrystal.

The structure of cocrystal 1 (1:1, CL-20/MTNI) was directly determined using single-crystal X-ray diffraction (SC-XRD) (Fig. S1 in supporting information). Cocrystal 1 was further characterized by powder X-ray diffraction (PXRD), infrared spectroscopy (IR), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), which showed that its morphology was completely different from pure raw materials.

2. Experimental

Caution: although we have encountered no difficulties in preparing a cocrystal CL-20/MTNI in this work, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions of these energetic materials involving scratching or scraping must be avoided!

2.1. Materials

CL-20 was provided by Liaoning Qingyang Chemical Industry Co. Ltd, China, and MTNI was prepared according to the published procedure of Lian et al. (2020) at North University of China. The other reagents used in this study were purchased from from Sinopharm Chemical Reagent Co. Ltd, China, without further purification.

2.2. Synthesis

A 1:1 mixture of ε-CL-20 (438 mg, 1 mmol) and MTNI (217 mg, 1 mmol) was added to ethanol (20 ml) and stirred until all the raw materials dissolved. The solvent was evaporated at room temperature, which yielded an orange–yellow cocrystal.

2.3. Single crystal X-ray diffraction

SC-XRD data for cocrystal 1 was collected on a D8 VENTURE with Mo Kα radiation (λ = 0.71073 Å). High-quality single crystal was selected and purged with a cooled nitrogen gas stream at 140 K throughout the data collection. Olex2 software (Dolomanov et al., 2009) was used as a viewer and a GUI to launch SHELXL. The structure was solved by the direct methods (SHELXL-2015 software (Sheldrick, 2015a,b) and refined by the full-matrix-block least-squares method on F² with anisotropic displacement parameters for all non-hydrogen atoms.

2.4. Morphology

The morphologies of the raw materials and cocrystal 1 were determined using a ZEISS MERLIN Compact SEM at 3 kV and 265 μA.

2.5. Powder X-ray diffraction

PXRD patterns were obtained at ambient temperature on a Rigaku Ultima IV powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The sample was placed onto a circular glass sample holder and covered with a glass slide. The sample was scanned in the range of 2θ from 5° to 80° in a continuous scan with a step size of 0.015° and a scan speed of 0.4 s per step.
2.6. Infrared spectroscopy

IR spectra were recorded in KBr pellets on a Bruker Model Vertex 80 FTS spectrometer.

2.7. Thermal analysis

DSC was performed on a METTLER DSC 3 instrument. The sample (~1 mg) was placed in a stainless steel high pressure crucible and heated from 30 to 300°C at heating rates of 10°C min⁻¹ in a nitrogen atmosphere at a flow rate of 50 ml min⁻¹.

2.8. Sensitivity test

Impact sensitivity and friction sensitivity were used to further evaluate the safety performance of energetic materials, which were determined using a BAM fall hammer apparatus and BAM friction tester, respectively.

2.9. Detonation property evaluation

The detonation velocity and detonation pressure of cocrystal 1 were calculated via empirical nitrogen equivalent equations (Hu et al., 2015).

The equation of detonation velocity is described as follows:

\[
D = 100M(695 + 1150\rho)(1.00x_{N\text{,}} + 0.64x_{H_2O} + 1.34x_{CO_2} + 0.72x_{CO} + 0.18x_{H_2} + 0.50x_{O_2} + 0.12x_C).
\]

Here, \(M\) represents the molar mass of explosive, \(\rho\) is the crystal density of explosive; 695 and 1150 are constants; 1.00, 0.64, 1.34, 0.72, 0.18, 0.50, 0.12 are the nitrogen equivalent coefficient of gaseous detonation products \(N_2, H_2O, CO_2, CO, H_2, O_2, C\) of explosive, respectively.

The equation of detonation pressure is described as follows:

\[
P = 1.060\left[\frac{100}{M}(1.00x_{N\text{,}} + 0.64x_{H_2O} + 1.34x_{CO_2} + 0.72x_{CO} + 0.18x_{H_2} + 0.50x_{O_2} + 0.12x_C)\right]^2 - 0.619.
\]

Here, 1.060 and 0.619 are constants.

3. Results and discussion

3.1. Single crystal X-ray diffraction

Cocrystal 1 crystallizes in the monoclinic space group \(P2_1/c\), and its asymmetric unit consists of one CL-20 molecule and one MTNI molecule. The full crystallographic data for cocrystal 1 have been deposited in the Cambridge Crystallographic Data Centre (CCDC number 2034034) and selected data are presented in Table 1.

The packing of the structure of cocrystal 1 is shown in Fig. 1. The CL-20 molecules and MTNI molecules are stacked together in a pocket-like style [Fig. 2(a)]; in this type of stacking, one MTNI molecule is surrounded by eight CL-20 molecules [Fig. 3(b)]. As shown in Fig. 3(a), the nitro, methylene and methyl groups of CL-20 and MTNI determine the negative and positive electrostatic potential (ESP) regions, respectively, without any extraordinarily red or blue regions on the molecular surface. That is, the molecular surfaces of CL-20 and MTNI do not have especially high negative or positive ESP or high polarity. ESP was determined using Materials Studio (Accelrys, 2020). This indicated that the CL-20 and MTNI molecules were neither a strong hydrogen...
bonding donor (HBD) nor a strong hydrogen bonding acceptor (HBA). However, O and N atoms with high polarity or high negative ESP in the MTNI molecule, mostly belonged to N=O and C==N groups as strong HBAs [Fig. 3(b)], which could easily form C—H···O and C—H···N interactions by contacting the C—H groups of CL-20. By analyzing the crystal structure, the formation of cocrystal 1 mainly depended on two main types of intermolecular interactions. The first type of intermolecular interactions consists of CH···O and CH···N HB interactions with bond distances ranging from 2.487 to 2.742 Å and 2.342 to 2.551 Å, respectively [Fig. 3(b)], which are all weaker hydrogen bonds. A similar situation also occurred in cocrystals of a CL-20/nitro-rich heterocyclic explosive (Tan et al., 2019; Anderson et al., 2016; Yang et al., 2018). The second type of intermolecular interaction is the NO2−π interaction which is formed by the nitro groups of CL-20 and the electron-deficient heterocyclic rings of MTNI with the bond lengths ranging from 3.134 to 3.473 Å [Fig. 3(c)].

3.2. Morphology

Fig. 4 shows SEM images of the morphologies of cocrystal 1, ε-CL-20 and MTNI. The differences in morphology revealed the different microstructures between them. Cocrystal 1 kept its original morphology (bulk crystal, 5 × 5 × 2 mm) after being sealed and stored in a vial for 14 months, which showed the stability of cocrystal 1.

3.3. Powder X-ray diffraction

As shown in Fig. 5, the PXRD pattern of cocrystal 1 was significantly different from that of ε-CL-20, MTNI and their mechanical mixture [ε-CL-20 and MTNI (molar ratio 1:1) were ground in water, stirred and mixed evenly, filtered and vacuum dried to obtain the mechanical mixture CL-20/MTNI]. Compared with the raw material, some new sharp peaks were observed in the cocrystal 1 pattern in the 2θ range of 10–35°. Meanwhile, some main peaks at 11–14° of ε-CL-20 and MTNI disappeared in the pattern of cocrystal 1. Therefore, cocrystal 1 could be easily distinguished from the raw materials by the PXRD pattern. Furthermore, the sharp peak of the mechanical mixture at 12.4°, which was the main peaks of the raw materials, disappear in the cocrystal diffraction pattern. It indicated that cocrystal 1 was not a simple mechanical mixture of ε-CL-20 and MTNI.
3.4. Infrared spectroscopy

The peak at 3016.5 cm$^{-1}$ of the infrared spectrum for $\varepsilon$-CL-20 and the mechanical mixture disappeared in cocrystal 1 (Fig. 6). Meanwhile, some new peaks at 3226.7, 1745.5 and 1456.2 cm$^{-1}$ appeared in cocrystal 1, but these peaks were not found in $\varepsilon$-CL-20, MTNI or their mechanical mixture. The infrared spectrum also revealed that cocrystal 1 was not a simple mixture of $\varepsilon$-CL-20 and MTNI.

3.5. Thermal analysis

The thermal properties of cocrystal 1, $\varepsilon$-CL-20, MTNI and the mechanical mixture were tested by using DSC (Fig. 7), which showed that cocrystal 1 had no melting point, but the melting point of the mechanical mixture of $\varepsilon$-CL-20/MTNI was 86.0°C, which may be due to the strong intermolecular interaction of cocrystal and weaker intermolecular interaction of the mechanical mixture. Besides, the descending order of decomposition temperatures were $\varepsilon$-CL-20, MTNI, mechanical mixture and cocrystal 1 whose values were 252.2, 251.2, 223.0 and 216.2°C, respectively, (Table 2) which showed that they have good thermal stability, but the thermal stability of cocrystal 1 is worse than that of the raw materials and the mechanical mixture.

3.6. Sensitivity test

The impact sensitivity and friction sensitivity of cocrystal 1, $\varepsilon$-CL-20 and MTNI are listed given in Table 3. The impact sensitivity of cocrystal 1 is 10 J, which is between the impact sensitivities of pure $\varepsilon$-CL-20 (4 J) and MTNI (13 J), but slightly higher than that of HMX (6 J) and RDX (8 J). The friction sensitivity of cocrystal 1 is 360 N, which is markedly higher than those of pure $\varepsilon$-CL-20 (95 N), HMX (120 N) and RDX (120 N), but equal to that of MTNI (360 N). The impact sensitivity and friction sensitivity results showed that cocrystal 1 has an expected low impact sensitivity.

Table 2
Melting points and decomposition temperatures for $\varepsilon$-CL-20, MTNI, cocrystal 1, and mechanical mixture $\varepsilon$-CL-20/MTNI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point (°C)</th>
<th>Decomposition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$-CL-20</td>
<td>-</td>
<td>252.2</td>
</tr>
<tr>
<td>MTNI</td>
<td>86.3</td>
<td>251.2</td>
</tr>
<tr>
<td>Cocrystal 1</td>
<td>-</td>
<td>216.2</td>
</tr>
<tr>
<td>Mechanical mixture $\varepsilon$-CL-20/MTNI</td>
<td>86.0</td>
<td>223.0</td>
</tr>
</tbody>
</table>

Table 3
Impact sensitivity, friction sensitivity and detonation properties for $\varepsilon$-CL-20, MTNI, cocrystal 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Impact sensitivity (J)</th>
<th>Friction sensitivity (N)</th>
<th>Density† (g cm$^{-3}$)</th>
<th>Detonation velocity‡ (m s$^{-1}$)</th>
<th>Detonation pressure‡ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$-CL-20</td>
<td>4.0</td>
<td>95</td>
<td>2.04</td>
<td>9767</td>
<td>44.83</td>
</tr>
<tr>
<td>MTNI</td>
<td>13</td>
<td>360</td>
<td>1.78</td>
<td>8360</td>
<td>30.49</td>
</tr>
<tr>
<td>Cocrystal 1</td>
<td>10</td>
<td>360</td>
<td>1.89 (140K)</td>
<td>9093</td>
<td>37.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.85 (298.15 K)‡</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMX</td>
<td>6</td>
<td>120</td>
<td>1.90</td>
<td>9180</td>
<td>38.26</td>
</tr>
<tr>
<td>RDX</td>
<td>8</td>
<td>120</td>
<td>1.82</td>
<td>8887</td>
<td>35.05</td>
</tr>
</tbody>
</table>

† Density at room temperature. ‡ The detonation velocity and detonation pressure are calculated by the empirical nitrogen equivalent equations. § The density at room temperature is calculated by $\rho_{298.15K} = \rho_0[1 + \alpha_\rho(298.15 - T)]$, $\alpha_\rho = 1.5 \times 10^{-4}$ K. This formula comes from Fischer et al. (2014).
3.7. Detonation property evaluation

Density is one of the key factors affecting the explosive performance of energetic materials. The crystal density of cocrystal 1 is 1.89 g cm\(^{-3}\) at 140 K (Table 3, 1.85 g cm\(^{-3}\) at 298.15 K), which is higher than that of MTNI (1.78 g cm\(^{-3}\) at 298 K) and a CL-20/TNT cocrystal (1.84 g cm\(^{-3}\) at 296 K) (Bolton & Matzger, 2011), but substantially lower than that of \(\varepsilon\)-CL-20 (2.04 g cm\(^{-3}\)). To further evaluate the explosive performance, the detonation velocity and detonation pressure of cocrystal 1, \(\varepsilon\)-CL-20 and MTNI were calculated using the empirical nitrogen equivalent equations (Hu et al., 2015) at 298.15 K; these values were approximated. As shown in Table 3, the detonation velocity and detonation pressure of cocrystal 1 were 9093 m s\(^{-1}\) and 37.46 GPa, respectively, which were substantially lower than those of \(\varepsilon\)-CL-20 (9767 m s\(^{-1}\), 44.83 GPa), but significantly higher than those of MTNI (8360 m s\(^{-1}\), 30.49 GPa). Meanwhile, the detonation velocity and detonation pressure of cocrystal 1 were between HMX (9180 m s\(^{-1}\), 38.26 GPa) and RDX (8877 m s\(^{-1}\), 35.05 GPa), but its sensitivity performance was better than for HMX and RDX, which indicated that cocrystal 1 is the desired high-energy and low-sensitivity explosive.

4. Conclusion

In summary, an energetic cocrystal composed of \(\varepsilon\)-CL-20 and MTNI (molar ratio 1:1) was synthesized and characterized. The decomposition temperature of cocrystal CL-20/MTNI was 216.2°C, which was lower than the decomposition temperature of CL-20 and MTNI. The impact sensitivity, friction sensitivity, detonation velocity and detonation pressure of cocrystal CL-20/MTNI were 10 J, 360 N, 9093 m s\(^{-1}\) and 37.46 GPa, respectively. Its explosive performance is comparable to HMX, but its sensitivity performance is significantly better than HMX.

Acknowledgements

This work was supported by the Military Chemistry and Pyrotechnics National Defense Specialty Fund for North University of China. We thank the Center of Testing and Analysis, Chinese Academy of Sciences, Shanghai Institute of Materia Medica and North University of China for support. We also gratefully acknowledge the support of Zhang Feiyan at the Shiyanjia Laboratory, China.

References


