

Synthesis, Structural Investigation, Thermal Decomposition, and Properties of a Cocrystal Energetic Perchlorate Amine Salt

P. Ma^a, L. Zhang^a, Sh.-G. Zhu^a, and H.-H. Chen^a

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Abstract: The molecular and crystal structure of a cocrystal energetic material (ethylenediamine triethylenediamine tetraperchlorate) is determined by means of the x-ray diffraction analysis. The compound crystallizes in the orthorhombic system of the Cmc21 space group with cell dimensions $a = 8.1030 \pm 0.0016$ Å, $b = 24.725 \pm 0.005$ Å, and $c = 10.195 \pm 0.002$ Å. The thermal decomposition mechanism of the title compound is studied by applying the Kissinger's and Ozawa's methods. Sensitivity tests reveal that the title compound has a sensitive nature.

Keywords: Cocrystal, crystal structure, perchlorate amine.

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INTRODUCTION

Cocrystal engineering (simultaneous crystallization of individual substances) is an emerging research area mainly in drug design. This emerging technology allows modifying the composition of matter and physicochemical properties of molecular compounds without breaking or forming a covalent bond. Most of the existing literature on cocrystal formation focuses on the exploitation of hydrogen bonding schemes and π - π interactions [1–5]. Because of the molecular recognition in cocrystal engineering (selective coupling of molecules owing to incovalent interactions), it is possible to design energetic materials from various chemical compounds. For example, triacetone triperoxide (TATP) possesses a high power, but it is very sensitive to shocks. Therefore, cocrystallization is a better way for this kind of materials to reach higher stability and lower sensitivity.

Here, we report a new kind of a cocrystal energetic material: ethylenediamine (EN) as the smallest one of polyamines behaves as a bidentate ligand that can form two coordinative bonds with metal atoms through the lone pair of electrons on both nitrogen atoms [6]. Be-

cause of the strong coordination capacity of EN, some new energetic materials exist with EN as a ligand [7–9]. The thermal analysis for this type of materials was performed in [10–13]. Triethylenediamine is used for supramolecular chemistry, which invokes great attention all over the world [14–16].

Churchill [16] pointed out some organic perchlorate compounds like tropylium perchlorate, dipyridinesilver (I) perchlorate, and ferrocenium perchlorate as potentially promising energetic materials. In order to investigate the new kind of perchlorate amine salts, which could be used as energetic materials, we synthesized a new material, which contains ethylenediamine and triethylenediamine. The crystal structure of the new energetic material, as well as its thermal decomposition and sensitivity were investigated.

EXPERIMENTAL

The title compound is an energetic material and tends to explode under certain condition. Appropriate safety precautions, such as safety glasses, face shields, leather coat, and ear plugs should be used.

^aSchool of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094 P.R. China; mapengcn@yahoo.com

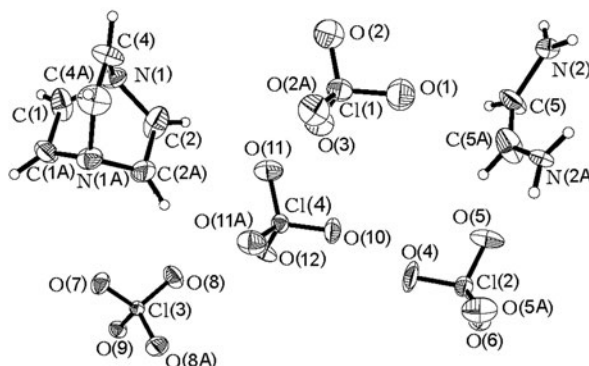
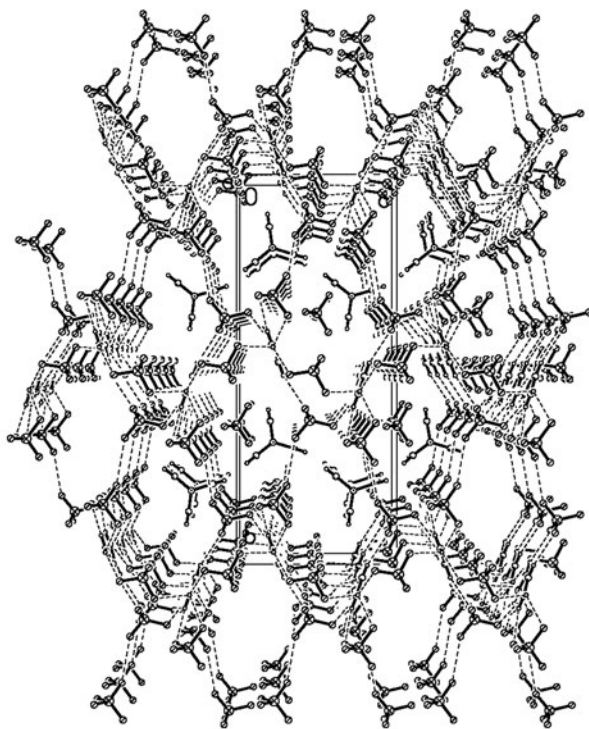
Table 1. Crystal data and structure refinement for the title compound

Empirical formula	C ₈ H ₁₄ O ₁₆ N ₄ Cl ₄
Formula weight	564.03
Temperature, K	293 ± 2
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	Cmc21
<i>a</i> , Å	8.1030 ± 0.0016
<i>b</i> , Å	24.725 ± 0.005
<i>c</i> , Å	10.195 ± 0.002
α , deg	90.00
β , deg	90.00
γ , deg	90.00
Volume, Å ³	2042.5 ± 0.7
<i>z</i>	4
Crystal size, mm	0.30 × 0.20 × 0.20
Density (calculated), g/cm ³	1.834
<i>F</i> (0 0 0)	1 144
Absorption coefficient	0.668
Range for data collection, deg	2.52 div 25.26
Goodness-of-fit on <i>F</i> ²	1.067
<i>R</i> indices (all data)	0.0662

All chemical reagents and solvents of the analytical grade were bought from a reagents company and used as supplied. Differential scanning calorimetry (DSC) was performed on a model Pyris-1 differential scanning calorimeter in a dry oxygen-free nitrogen as an atmosphere with a flow rate of 20 ml/min. Samples of about 0.5 mg were sealed in aluminum pans for DSC.

Synthesis

The sample used in this work was prepared by the following method: 5.0 g of ethylenediamine and 9.4 g of triethylenediamine were charged into a glass reactor containing 50 ml of distilled water. The mixture was mechanically stirred. 48 g of perchloric acid were added dropwise to the glass reactor. The addition of the reactant resulted in a severely exothermic reaction. The solution became clear from the turbidity, and its temperature increased quickly. The temperature of the solution should be kept below 70°C; otherwise, the solution would turn to yellow and would affect the quality of the product. The solution obtained was stirred for ad-

**Fig. 1.** Molecular unit for SY.**Fig. 2.** Crystal packing for the title compound.

ditional 30 min. Then the cooling system was removed to let the reaction reach room temperature on stirring up to 1 h until a white precipitate of ethylenediamine triethylenediamine tetraperchlorate (SY) was obtained. The crystals were washed three times with ethyl alcohol (3 × 50 ml) and dried at 60°C. The yield was about 94% for the first time. The remaining mother liquor could be collected for subsequent synthesis: 50 mL of the mother liquor was charged to the glass reactor in place of distilled water, and the same operations as described above were performed.

X-ray Crystallography

For the title compound, the displacement ellipsoid plot with the numbering scheme is shown in Fig. 1, and a perspective view of the crystal packing in the unit cell is shown in Fig. 2. The intensity data of the title compound having the edges of $0.30 \times 0.20 \times 0.20$ mm, which were collected at 293 ± 2 K by using a four-circle CAD4/PC (graphite-monochromatized MK_{α} -radiation, $\lambda = 0.71073$ Å), are presented in Table 1. The data were obtained in the $\omega/2\theta$ scan mode, with three standard reflections measured every 120 min. Data reduction was carried out with the XCAD-4 program. An absorption correction based on the PSI-scan method was applied. The structure was solved by direct methods and refined by the full-matrix least-squares technique on F^2 with anisotropic thermal parameters for all non-hydrogen atoms by the SHELXS97 [17] and SHELXL97 [18] programs. All hydrogen atoms were located from the difference Fourier map and refined isotropically. Detailed information concerning crystallographic data collection and structure refinement is summarized in Table 1.

RESULTS AND DISCUSSION*Structure Description*

Figure 1 shows the molecular unit for SY. Selected bond lengths and bond angles of the title compound are listed in Table 2. The hydrogen bond lengths and bond angles are listed in Table 3. The molecular unit contains one ethylenediamine cation, one triethylenediamine cation, and four perchlorate anions.

SY is crystallized with one ethylenediamine cation, triethylenediamine cation, and perchlorate anion. There is no evidence of covalent bonding interactions between the perchlorate anion and ethylenediamine and triethylenediamine cations; however, there are close contacts, probably indicative of intermolecular hydrogen bonding and potentially weak (N—H...O) intermolecular interactions, as is shown in Table 3. The hydrogen bond is formed among the ethylenediamine cation, triethylenediamine cation, and perchlorate anion.

Hydrogen bonds are often employed in cocrystal design due to their inherently robust and directional nature. In the SY structure, the ethylenediamine cation, triethylenediamine cation, and perchlorate anion are all good hydrogen bond donors and acceptors; therefore, we can argue that hydrogen bonding plays an important role in cocrystal formation. From the general hydrogen

Table 2. Selected bond lengths and bond angles for SY

Bond lengths, Å	
N(1)—C(1)	1.460 ± 0.008
N(1)—C(2)	1.489 ± 0.010
N(1)—C(4)	1.513 ± 0.009
C(5)—C(5A)	1.345 ± 0.014
Cl(1)—O(1)	1.438 ± 0.008
Cl(1)—O(2A)	1.385 ± 0.006
Cl(2)—O(4)	1.352 ± 0.006
Cl(2)—O(5)	1.343 ± 0.005
Cl(3)—O(7)	1.414 ± 0.006
Cl(3)—O(8)	1.435 ± 0.004
Cl(4)—O(10)	1.379 ± 0.006
Cl(4)—O(11)	1.412 ± 0.005
N(2)—C(5)	1.472 ± 0.007
C(1)—C(1A)	1.506 ± 0.014
C(2)—C(2A)	1.544 ± 0.016
C(4)—C(4A)	1.411 ± 0.015
Cl(1)—O(2)	1.385 ± 0.006
Cl(1)—O(3)	1.363 ± 0.005
Cl(2)—O(5A)	1.343 ± 0.005
Cl(2)—O(6)	1.460 ± 0.006
Cl(3)—O(8A)	1.435 ± 0.004
Cl(3)—O(9)	1.432 ± 0.005
Cl(4)—O(11A)	1.412 ± 0.005
Cl(4)—O(12)	1.463 ± 0.005
Bond angles, deg	
C(1)—N(1)—C(2)	105.1 ± 0.6
C(1)—N(1)—C(4)	108.0 ± 0.6
N(2)—C(5)—C(5A)	131.4 ± 0.3

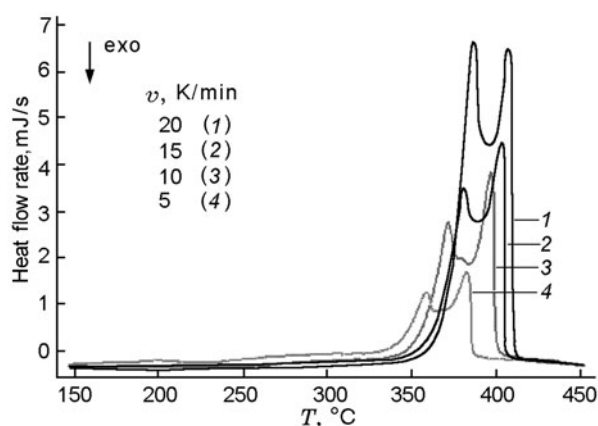
bonding rules [14], the best hydrogen bond donor tends to interact with the best hydrogen bond acceptor. In the SY crystal structure, hydrogen bonding between the donor N—H and acceptor O is most probable.

Thermal Decomposition

In order to investigate the thermal decomposition of SY, the DSC and thermogravimetric (TG) experiments were carried out. The DSC and TG curves of the title compound at heating rates of 5, 10, 15, and 20 K/min in an N₂ gas flow are illustrated in Fig. 3 and Table 4. It can be seen from the DSC curve that decom-

Table 3. Intermolecular interaction distances and angles for SY

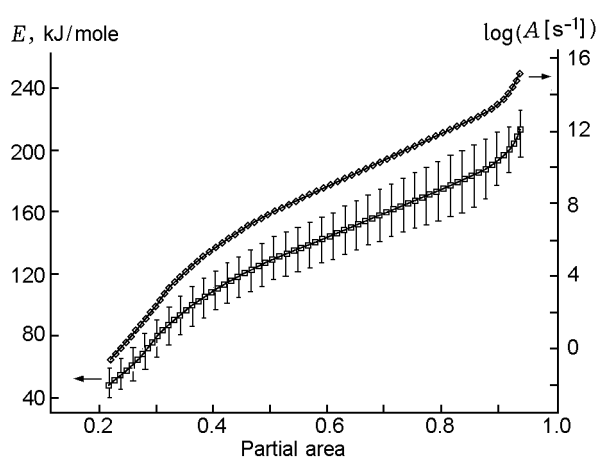
Donor—H... acceptor	D—H, Å	H...A, Å	D...A, Å	D—H...A, deg
N(1)—H(1A) ... O(3)	1.047	2.268	3.159	141.8
N(1)—H(1B) ... O(4)	1.047	2.260	3.150	141.7
N(1)—H(1B) ... O(3)	1.047	2.268	3.159	141.7
N(1)—H(1B) ... O(4)	1.047	2.260	3.150	141.8
N(2)—H(2C) ... O(2)	1.047	2.494	2.985	121.2
N(2)—H(2C) ... O(8)	1.047	2.187	3.072	141.3
N(2)—H(2C) ... O(12)	1.047	2.306	2.985	121.2
N(2)—H(2D) ... O(11)	1.042	2.425	2.988	112.8

**Fig. 3.** DSC curves of the title compound at different heating rates v .**Table 4.** Peak temperatures of the first exothermic stage at different heating rates of the SY sample

v , K/min	T , K
5	657.8
10	671.6
15	677.4
20	662.3

position of the title compound occurs in the temperature range of 320–415°C with three exothermic stages. The exothermic process starts at 325–375°C and reaches the peak temperature at 350–390°C. Kissinger's and Ozawa's methods were applied to study the kinetic parameters of the first exothermic stage, based on the DSC curve obtained under the condition of static air at heating rates of 5, 10, 15, and 20 K/min. The equations derived by Kissinger and Ozawa have the form

$$\ln \frac{\beta}{T_{\max}^2} = \ln \frac{RA}{E} - \frac{E}{RT_{\max}}$$

**Fig. 4.** Activation energy and pre-exponential factor of the first stage calculated by Ozawa's method.

$$\ln \beta_i = \ln \frac{AE}{RG(\alpha)} - 5.3308 - 1.0516 \frac{E}{RT}$$

where β [K/min] is the linear heating rate, R is the gas constant equal to 8.314 J/(mole·K), A [s^{-1}] is pre-exponential factor, α is the conversion rate, $G(\alpha) = \frac{AE}{\beta R} P(u)$, and $P(u) = \int_{\infty}^u \frac{-e^{-u}}{u^2} du$. The activation energy and the pre-exponential factor determined by Ozawa's method are shown in Fig. 4. The activation energy determined by Kissinger's method was 168.64 kJ/mole for the first stage and 198.8 kJ/mole for the second stage.

Sensitivity Test

The impact sensitivity was determined by a Kast drop hammer apparatus. A 30-mg SY sample was compacted in a steel cap and was hit by a 10-kg drop hammer. The 50% firing height is 9.5 cm. Thus, the impact sensitivity of the title compound (9.5 cm) is lower than that of PETN (4.4 cm) under the same conditions.

The friction sensitivity was determined by a pendulum apparatus. When a 20-mg SY sample was compressed between two steel poles with mirror surfaces at a pressure of 1.05 MPa and was hit horizontally with a 1.5-kg hammer deflected at 60° from the vertical axis, the firing probability was 56%. The flame sensitivity was tested according to the method described in [19]. A 20-mg SY sample was compacted in a copper cap under the pressure of 20 MPa and was ignited by a black powder pellet located right above the sample. The 50 % firing height is 7.3 cm.

CONCLUSIONS

A new type of a cocrystal perchlorate amine salt (SY) has been prepared and characterized. Its structure belongs to the orthorhombic system, and the group space is Cmc21. The DSC analysis of the title compound shows that there are two exothermic decomposition stages in the temperature range from 300 to 420°C. The sensitivity results show that the title compound is a promising explosive.

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