



Synthesis and characterization of an energetic compound $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$ and effect on thermal decomposition of ammonium perchlorate

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ARTICLE INFO

Article history:

Received 9 April 2011

Received in revised form

17 September 2011

Accepted 19 September 2011

Available online 22 September 2011

Keywords:

1-methyltetrazole

Crystal structure

Thermal decomposition

Non-isothermal kinetics

Ammonium perchlorate

ABSTRACT

An energetic coordination compound $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$ has been synthesized by using 1-methyltetrazole (Mtta) as ligand and its structure has been characterized by X-ray single crystal diffraction. The central copper (II) cation was coordinated by four O atoms from two Mtta ligands and two N atoms from two NO_3^- anions to form a six-coordinated and distorted octahedral structure. 2D supermolecular layer structure was formed by the extensive intermolecular hydrogen bonds between Mtta ligands and NO_3^- anions. Thermal decomposition process of the compound was predicted based on DSC and TG-DTG analyses results. The kinetic parameters of the first exothermic process of the compound were studied by the Kissinger's and Ozawa-Doyle's methods. Sensitivity tests revealed that the compound was insensitive to mechanical stimuli. In addition, compound was explored as additive to promote the thermal decomposition of ammonium perchlorate (AP) by differential scanning calorimetry.

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1. Introduction

Research in the field of highly energetic materials is nowadays directed toward the synthesis of simple molecules with high energy, high density, high heat resistance, and low sensitivity [1]. Recently, considerable attention has been paid in the study of tetrazoles and their derivatives as ligands to metals due to their varied structures and energetic properties [2–6]. 1-methyltetrazole (Mtta), as a simple tetrazole derivative, has the higher nitrogen content – 66.6%. For this ligand, researchers focus only on the magnetic properties and relevant theory investigation [7–10]. There is no literature about its energetic property so far.

Ammonium perchlorate (AP) is the common oxidizer in composite solid propellants, and the thermal decomposition characteristics of AP directly influence the combustion behavior of solid propellants [11,12]. Many effective combustion catalysts on the thermal decomposition of AP, such as metal oxides, which are not nitrogen-rich or energetic compounds, have been reported [13–16].

Copper(II) exhibits a good ability when coordinating with different kinds of ligand, and is more environmental friendly compared with the toxic heavy metal ions as lead and mercury. Therefore, in this paper we report the synthesis and structure of $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$. Furthermore, thermal decomposition process,

the kinetic parameters of the first exothermic process of the compound, sensitivity and the catalytic performance toward thermal decomposition of AP are explored.

2. Experimental

General caution: Mtta and the title compound are energetic materials and tend to explode under certain conditions. Appropriate safety precautions (safety glasses, face shields, leather coat and ear plugs) should be taken, especially when the compound is prepared on a large scale.

2.1. Materials and instruments

All reagents (analytic grade) were purchased commercially and used without further purification.

Elemental analyses were carried out using an instrument of Vario EL III analyzer. Infrared (IR) spectra drawn at regular intervals were recorded on a Bruker FTIR instrument as KBr pellets. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a Netzsch STA 449C instrument and a CDR-4P thermal analyzer of Shanghai Balance Instrument factory, respectively, using dry oxygen-free nitrogen as atmosphere with the flowing rate of 10 ml/min. The sample of about 0.5 mg was held in platinum pans for TG and sealed in aluminum pans for DSC. The sensitivity to impact stimuli was determined by fall hammer apparatus applying standard staircase method using a 2 kg drop weight

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

Empirical formula	C ₄ H ₈ CuN ₁₀ O ₆
Formula weight	355.74
Crystal system	P2(1)/c
Space group	Monoclinic
Temperature (K)	273(2)
a (Å)	10.156(2)
b (Å)	6.389(1)
c (Å)	9.820(2)
α (°)	90
β (°)	103.74(3)
γ (°)	90
V (Å ³)	618.9(2)
Z	2
Density, calculated (g cm ⁻³)	1.909
μ (mm ⁻¹)	1.817
F(000) Å	358
θ range for data collection (°)	2.06 to 26.10
Independent reflections	1089
Goodness-of-fit on F ²	1.020
Final R indices [I > 2σ(I)]	R ₁ = 0.0745, wR ₂ = 0.1820
R indices (all data)	R ₁ = 0.1067, wR ₂ = 0.2066
Largest peak and hole (e Å ⁻³)	0.739 and -1.132

and the results were reported in terms of height for 50% probability of explosion ($h_{50\%}$) [17]. The friction sensitivity of the compound was determined on a Julius Peter's apparatus by following the BAM method [18].

2.2. Synthesis

Cu(NO₃)₂·3H₂O (0.242 g, 1.0 mmol) was added to a solution of MttA (0.084 g, 1.0 mmol) in ethanol (20 ml) with stirring at room temperature. After keeping the mixture for 5 days at room temperature, the resulting blue block-like crystals were filtered off, washed with ethanol and then diethyl ether, and air dried (ca. 42% yield based on Cu). Anal. Calcd. (%) for Cu₄H₈N₁₀O₆: C, 13.51; H, 2.27; N, 39.38. Found: C, 13.59; H, 2.35; N, 39.42. IR data (KBr pellet, cm⁻¹): 3320s, 3261s, 3065s, 2970s, 2923s, 1648s, 1552s, 1427m, 1382s, 1103m, 1082m, 871w, 763m, 741w, 652w, 616w.

2.3. X-ray crystallography

The single crystal X-ray experiment was performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) using ω and φ scan mode. The single-crystal structure of compound was solved by direct methods and refined with full-matrix least-squares refinements based on F² using SHELXS 97 [19] and SHELXL 97 [20]. All non-H atoms were located using subsequent Fourier-difference methods. In all cases hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Other details of crystal data, data collection parameters and refinement statistics were given in Table 1. Selected bond lengths and bond angles of the compound were listed in Table 2.

3. Results and discussion

3.1. Structure description

Single-crystal analysis shows the compound crystallizes in monoclinic space group P2(1)/c and exists as a two-dimensional superamolecular layer. Fig. 1 shows the molecular unit of Cu(MttA)₂(NO₃)₂ with the atom labeling scheme. As shown in Fig. 1, the coordination geometry around Cu(II) ion can be described as a distorted octahedron, of which the equatorial plan is defined by four oxygen atoms (O1, O2, O1A and O2A) from two coordinated NO₃⁻ anions and the apical positions are occupied by two nitrogen

Table 2
Selected bond lengths (Å) and bond angles (°).

Cu(1)–N(4)	1.967(6)
Cu(1)–N(4)#1	1.967(6)
Cu(1)–O(1)#1	2.004(5)
Cu(1)–O(1)	2.004(5)
Cu(1)–O(2)	2.638(5)
O(1)–N(5)	1.288(7)
O(3)–N(5)	1.222(7)
O(2)–N(5)	1.226(7)
N(4)–Cu(1)–N(4)#1	180.0(1)
N(4)–Cu(1)–O(1)#1	89.1(2)
N(4)#1–Cu(1)–O(1)#1	90.9(2)
N(4)–Cu(1)–O(1)	90.9(2)
N(4)#1–Cu(1)–O(1)	89.1(2)
O(1)#1–Cu(1)–O(1)	180.0(3)
N(5)–O(1)–Cu(1)	108.5(4)
N(3)–N(4)–Cu(1)	124.2(5)
C(1)–N(4)–Cu(1)	129.0(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z+1.

atoms (N4 and N4A) from two MttA ligands. The average of Cu–O bond is in the range 2.004(5)–2.639(3) Å and the Cu–N bond length is 1.967(6) Å.

Furthermore, the molecule unit as showed is further extended into a 2D superamolecular layer through hydrogen bonding interactions, which C1 and C2 atoms from the molecule unit act as two hydrogen-bonding donors to interact with acceptors of O2 and O3 atoms from the adjacent molecule, with 3.183(9) Å for C(1)–H(1)···O(2); 3.311(1) Å for C(2)–H(2A)···O(3), as shown in Fig. 2.

3.2. Thermal decomposition

The DSC and TG-DTG curves under the linear heating rate of 10 °C/min with nitrogen atmosphere are shown in Figs. 3 and 4 to demonstrate the thermal decomposition processes of Cu(MttA)₂(NO₃)₂. In the DSC curve, there are two intense exothermic processes from 265 to 480 °C. Because two intense exothermic decomposition processes occur successively,

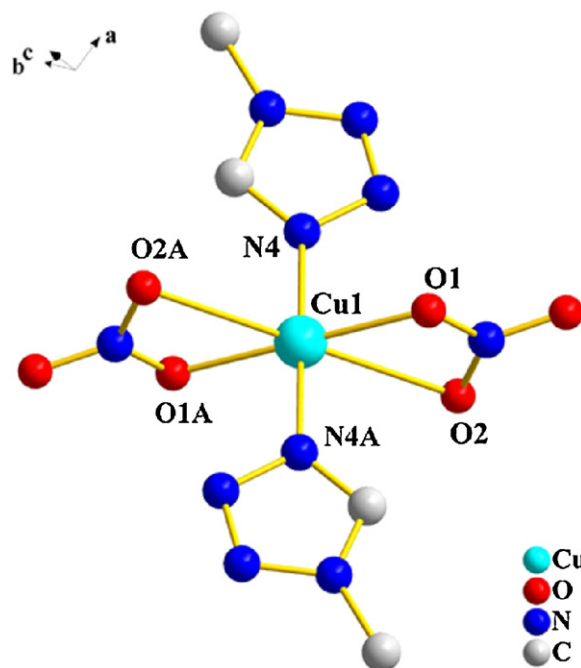


Fig. 1. Molecular unit and labeling scheme for the compound, H atoms were omitted for clarity.

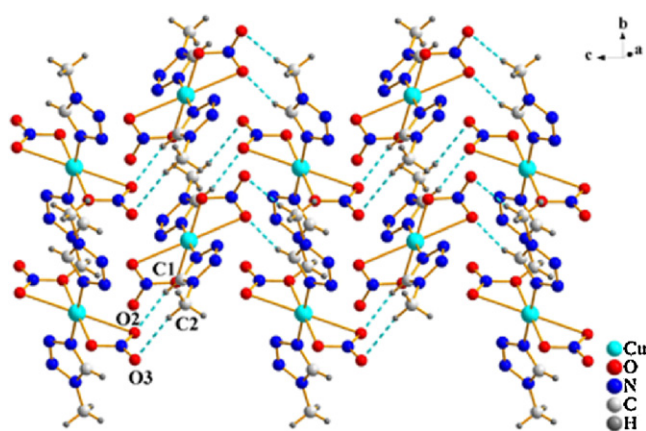


Fig. 2. 2D supermolecular layer of the compound.

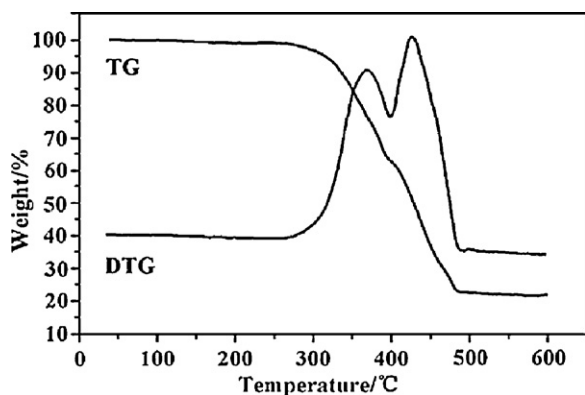


Fig. 3. TG-DTG curve of the compound.

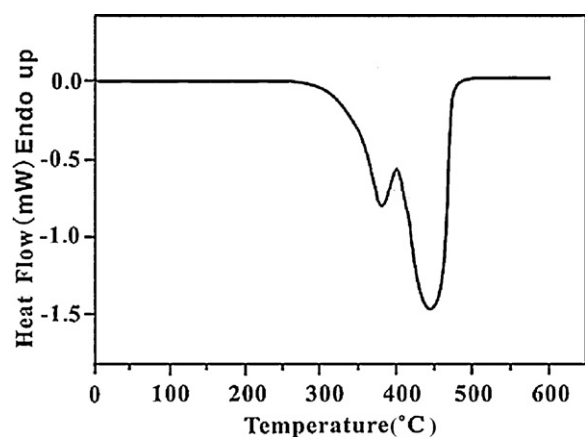


Fig. 4. DSC curve of the compound.

one decomposition process does not finish, and another occurs, the exothermic peaks cannot be separated, which form a wide exothermic peak. The first exothermic decomposition process occurs at 265 °C, and ends at about 400 °C; the second exothermic decomposition process occurs at the same time and ends at about 480 °C.

In the TG-DTG curves, there are two main successive mass loss stages from 265 to 480 °C, which correspond to the two intense exothermic processes in the DSC curve. The first weight loss stage starts at 265 °C, ends at 400 °C, and reaches the largest rate at 380 °C with weight loss percentage of 35.62%. This stage roughly coincides with the value of 34.86%, calculated for the loss of two coordinated NO_3^- anions. The second step from 400 to 480 °C is

Table 3

The peak temperatures of the first exothermic stage at different heating rates and the kinetic parameters.

Heating rates (°C/min)	Peak temperature (°C)
5	372.7
10	380.3
15	383.7
20	387.3
25	389.8
The calculation results by Kissinger's method	
E_k (kJ/mol)	327.4
$\text{Log } A_k$ (s^{-1})	24.38
Linear correlation coefficient (R_k)	0.9988
The calculation results by Ozawa–Doyle's method	
E_o (kJ/mol)	321.7
Linear correlation coefficient (R_o)	0.9989

considered as the break of the Mttal ligands and then the compound completely converts to the remainder CuO with weight loss percentage of 22.12%, which is in good agreement with the calculated value 22.36%. The remainder CuO is evidenced by X-ray powder diffraction analysis (Fig. 5, JPCDS 05-0661).

3.3. Non-isothermal kinetics analysis

In the present work, Kissinger's method [21] and Ozawa–Doyle's method [22,23] are widely used to determine the apparent activation energy (E) and the pre-exponential factor (A). The Kissinger and Ozawa–Doyle equations are as follows, respectively:

$$\frac{d \ln \beta / T_p^2}{d(1/T_p)} = -\frac{E}{R} \quad (1)$$

$$\log \beta + \frac{0.4567E}{RT_p} = C \quad (2)$$

where T_p is the peak temperature; A is the pre-exponential factor; E is the apparent activation energy; R is the gas constant; β is the linear heating rate and C is constant.

Based on the first exothermic peak temperatures measured at five different heating rates of 5, 10, 15, 20 and 25 °C/min, Kissinger's and Ozawa–Doyle's method are applied to study the kinetics parameters of the compound $\text{Cu}(\text{Mttal})_2(\text{NO}_3)_2$. From the original data, the apparent activation energy E_k and E_o , pre-exponential factor A_k and linear correlation coefficients R_k and R_o are determined and shown in Table 3.

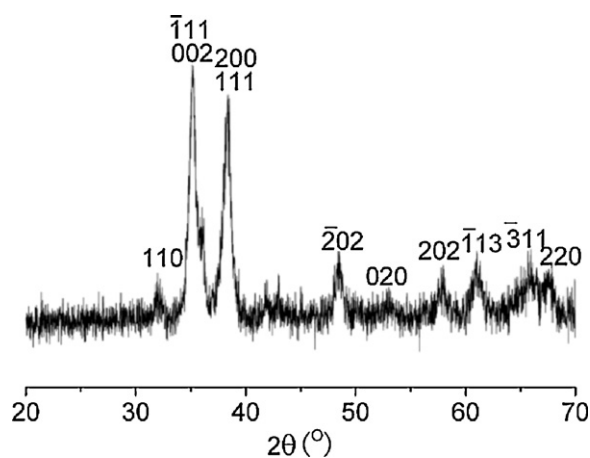


Fig. 5. X-ray powder diffraction for compound after decomposition.

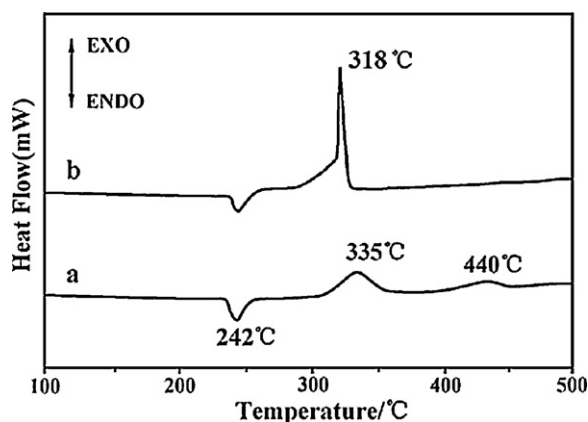


Fig. 6. DSC curves for AP (a) and AP + compound (b).

3.4. Sensitivity test

Impact sensitivity of $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$ was tested using a 2 kg drop hammer, and calculated value of H_{50} represented the drop height of 50% initiation probability. The impact sensitivity value (H_{50}) of the complex was 125 cm, which corresponds to the impact energy of 24.5 J. Under the same test condition, the impact sensitivity value (H_{50}) of TNT was 76.5 cm (15.0 J), which were consistent with the values of Ref. [24]. Therefore, the impact sensitivity of the title complex was lower than that of TNT.

Friction sensitivity of the complex was measured by applying a Julius Peter's machine. No friction sensitivity was observed up to 36 kg. The friction sensitivity of the complex was lower than that of RDX (12 kg) [25].

The results revealed that the title complex was insensitive to impact and friction stimuli.

3.5. Effects on thermal decomposition of ammonium perchlorate

Compound $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$ is explored as a promoter to the thermal decomposition of ammonium perchlorate (abbreviate AP), the key component of composite solid propellant. The performance of compound on the thermal decomposition of AP (compound and AP are mixed at a mass ratio of 1:3) is investigated by DSC measurement with a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere in the range of $100\text{--}500^\circ\text{C}$ with Al_2O_3 as reference. A total sample mass used is less than 1.0 mg for all runs. Fig. 6 shows the DSC curves of both AP and the mixture of AP with the title compound. The endothermic peak of AP at 242°C is due to the crystal transformation of AP from orthorhombic to cubic phase [26]. The exothermic peaks at 335 and 440°C are attributed to the partial decomposition of AP to form some intermediate product and then complete decomposition to volatile products [27,28], corresponding to the heat of 1.47 kJ/g and 0.68 kJ/g respectively. From Fig. 6b, we can see that the compound has no significant impact on the phase transition of AP. The two exothermic peaks merge to one and the peak temperature (318°C) is much lower than the exothermic peak temperature of pure AP (335°C). The sharp exothermic peak indicates a rapid decomposition process and the decomposition heat increases dramatically from 1.47 to 3.95 kJ/g. It can be inferred that the compound decomposes and releases much heat itself which enhances the total heat of the mixture, as well as the formation of metal at molecular level on propellant surface may contribute toward their catalytic effect [29]. Obviously, AP decomposition is accelerated in the presence of $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$.

4. Conclusion

An energetic coordination compound $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$ has been synthesized and structurally characterized. Its crystal structure belongs to trigonal system and the crystal structure data are as follows: $P2(1)/c$ space group, $a = 10.156(2)\text{Å}$, $b = 6.389(1)\text{Å}$, $c = 9.820(2)\text{Å}$, $\beta = 103.74(3)^\circ$ and $Z = 2$. The center Cu(II) ion is six-coordinated in a distorted octahedral geometry by two nitrogen atoms from two Mtta ligands and four oxygen atoms from two NO_3^- anions. The 2D layer structure is formed through hydrogen bonding interactions. Thermolysis exhibit the two intense exothermic decomposition of $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$ in the temperature range of $265\text{--}480^\circ\text{C}$, and the final decomposed residue is CuO. The sensitivity experimental results indicate that the insensitive nature of $\text{Cu}(\text{Mtta})_2(\text{NO}_3)_2$ to impact and friction stimuli. DSC experiment reveals that the compound accelerates the decomposition of AP and the present work can project the probable application of the compound in propellant field.

Acknowledgements

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (grant nos. 20873100, 21173168 and 21127004), the Natural Science Foundation of Shaanxi Province (grant nos. 2010JQ2007 and 2010JK882) and the Science Foundation of Northwest University (grant no. 09NW11).

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