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The Thermal Decomposition Mechanism and the Quantum Chemical Calculation of $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$

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Abstract: $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$ was prepared by adding magnesium carbonate hydroxide to the aqueous solution of 3-nitro-1,2,4-triazol-5-one (NTO). Its thermal decomposition mechanism was studied by DSC, TG/DTG and IR. The quantum chemical calculation on the title complex as a structure unit with the experimental geometry as starting values was carried out at B3LYP level with 6-31G basis set. The results show that the bonds between the coordinate waters and the Mg atom have certain extent covalent character. The net charges on nitrogen atoms of the NTO ring appear to be negative while the nitrogen atom on the nitro group ($—NO_2$) appears to be positive which indicates $—NO_2$ will lost first when the complex is heated to some uniform temperature and this result is in agreement with that of the thermal decomposition experiment.

Key words: physical chemistry; 3-nitro-1,2,4-triazol-5-one (NTO); magnesium complex; thermal decomposition mechanism; quantum chemical investigation

CLC number: O643; TQ564.2; O6-04 **Document code**: A

1 Introduction

3-nitro-1,2,4-triazol-5-one (NTO) is a high energy material with low sensitivity. As a low sensitivity energetic additive, NTO metal salts can be used as one of the components of intermolecular explosives and propellants. In recent years, much attention has been paid to the synthesis, crystal structure, thermal behavior and theoretical study on NTO metal salts[1~4]. We previously prepared, determined the crystal structure of NTO magnesium complex as $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$ and studied its thermodynamic properties[5], in this paper, we discussed its thermal behavior by DSC and TG/DTG techniques, the population analysis and the stability through theoretical calculation.

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2 Experimental

2.1 Thermal analysis

The DSC and TG/DTG experiments for the title compoundwere performed using a NETZSCH STA 449C under a nitrogen atmosphere, at a flow rate of 30 $mL \cdot min^{-1}$. The heating rate used was 15 $℃ \cdot min^{-1}$ from ambient temperature to 700 ℃.

2.2 Model and method of quantum chemical calculation

The analytical results indicate that the molecule is centrosymmetrical. The Mg atom is located at the center of the symmetry. Six oxygen atoms of six water molecules are combined with a Mg atom to form $[Mg(H_2O)_6]^{2+}$. Two NTO anions and two crystalline water molecules are combined by hydrogen bonds (see Figure 1).

Our experimental geometry was selected as the initial geometry (Fig. 1) and optimized using HF/6-31G and DFT-B3LYP/6-31G methods and the calculated framework group is $CI[O(Mg), X(C_4H_{18}N_8O_{14})]$. All calculations were carried out on a Legend P4 computer with G03w [6] program. In the result of the frequency calculation, there is no imaginary frequency which shows that our optimized geometry is the stable one.

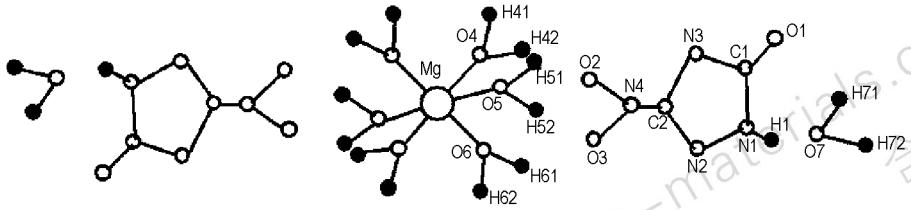

Fig. 1　The atomic number of $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$

3　Results and discussion

3.1　Thermogravimetric analysis data

DSC and TG/DTG curves are shown in Figs. 2 and 3 respectively. The results of thermal analysis indicate that the thermal decomposition of the title compound begins at 78 ℃ and ends at 695.2 ℃. The process can be divided into four stages as shown in the DTG curve. The first stage started from 78 ℃ to 143.8 ℃ with a mass loss of 17.83% corresponding to the loss of the 2 mol of crystallization H_2O and 2 mol of coordinated H_2O (theoretical mass loss is 16.89%) which can be confirmed by the structure solution. The bond distances between Mg-O4, Mg-O5 and Mg-O6 are 0.2057, 0.2046 and 0.2087 nm respectively. Obviously, the former is much shorter than the latter, so the bond of Mg-O6 and the symmetric coordinate bond are easier to be broken down when the compound is heated.

The second endothermic process is between 143.8 ℃ and 210.7 ℃. The mass loss is 16.06%, which coincides with the calculated value of 16.89%, corresponding to the loss of 4 mol water molecules.

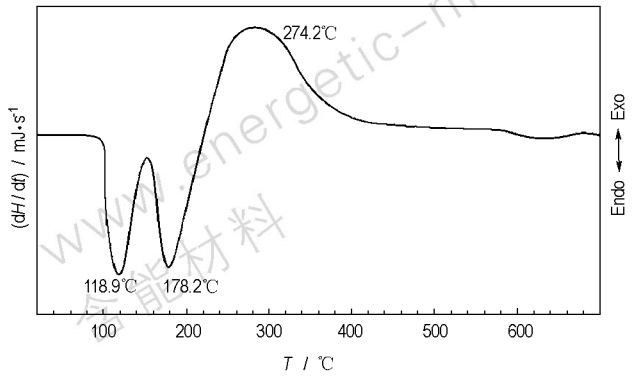

Fig. 2　DSC curve of the title compound at a heating rate of 15℃ · min^{-1}

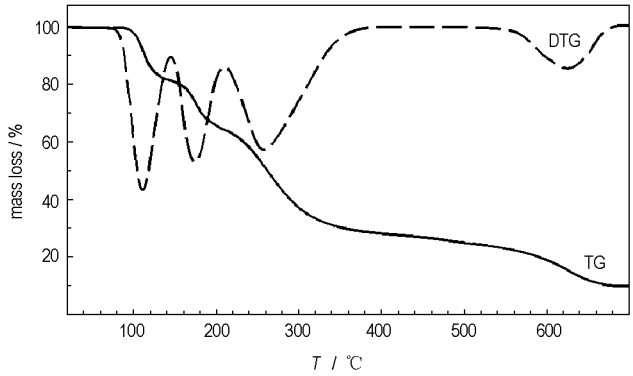

Fig. 3　TG/DTG curves of the title compound at a heating rate of 15℃ · min^{-1}

Further decomposition of the complex occurs between 210.7 ℃ and 416.5 ℃ accompanied by 35.36% mass loss, corresponding to the thermal decomposition of $Mg(NTO)_2$. In this process, plenty of gas was emerged and the IR spectrums of the residue showed that the decomposition remained were a mixture. The characteristic absorption peaks of $Mg(NCO)_2$ have formed at 2 245 and 1 188 cm^{-1}, the characteristic absorption peaks of $MgCO_3$ and polymers containing the—CO—NH—group have formed at 1 457, 852 cm^{-1} and 3 420, 1 617, 1 576 cm^{-1}. In the fourth-exothermal stage, the experimental value of the mass loss is about 17.10%. The characteristic absorption peak of MgO was found at 429 cm^{-1}. At the end of this stage, the residue amounted to 10.29%. This value is in good agreement with the calculated amount of 9.4%.

From the above analysis, the thermal decomposition of $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$ is postulated to proceed as follows:

$$[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O \longrightarrow [Mg(H_2O)_4](NTO)_2 \longrightarrow$$
$$Mg(NTO)_2 \longrightarrow MgCO_3 + Mg(NCO)_2 + \text{volatile substances} \longrightarrow MgO$$

3.2 Population analysis

Based on the composition of the molecule and the basis set we selected, there are 111 occupied molecule orbitals and 172 unoccupied molecule orbitals. Because the optimized geometry by HF method greatly deviates with the experimental result, the following discussion is based on the calculated result of DFT-B3LYP method. Table 1 shows the overlap contribution of the title compound.

Table 1 The population analysis of the title compound

bonds	B3LYP	bonds	B3LYP
Mg-O1	-0.000001	O6-H6B	0.205092
Mg-O2	0.005434	O3-H6B	0.057898
Mg-O3	0.005678	O6-H6A	0.244103
Mg-O4	0.105984	O3-H6A	0.000829
Mg-O5	0.104787	O6-O3	-0.023690
Mg-O6	0.108536	N1-H1	0.235815
Mg-O7	0.000000	O7-H1	0.079120
Mg-N4	-0.002321	N1-O1	-0.035567
O5-O2	-0.031562	O2-H5A	0.191535

Because the molecule of $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$ is centrosymmetrical, only a half of the data were listed in Table 1. From the population analysis, we can see that the overlap contribution between Mg atom and the oxygen atom of the carbonyl and Mg atom and the oxygen atom of the crystalline water are 0, which indicate that there are no bond interactions between them. The overlaps between Mg and O2, Mg and O3, Mg and N4 of the nitro group on the NTO anion are 0.005 434, 0.005 678 and -0.002 321 respectively show that these bonds are very weak. The population between Mg and the coordinate waters are 0.105 984, 0.104 787 and 0.108 536 indicate these bonds have certain extent covalent character. From the overlap value, we can see that the bonds between N1 and O1, O6 and O3, O5 and O2 are hydrogen bonds. However, from the structure solution[5], there are no hydrogen bonds between O5 and O2, this is because the calculated system is just a crystal cell without taking consideration the spatial arrangement.

3.3 The atomic charges

Net charges on atoms are listed in Table 2.

Table 2 Net charges of the title compound

atoms	charge/e	atoms	charge/e
C1	0.604347	O4	-0.820622
N1	-0.490735	O5	-0.824407
N2	-0.104607	O6	-0.800951
C2	0.522197	O7	-0.780404
N3	-0.387641	H41	0.421195
O1	-0.511772	H42	0.445265
N4	0.021462	H51	0.450193
O2	-0.371672	H52	0.420875
O3	-0.424799	H61	0.424157
H1	0.415802	H62	0.451018
		H71	0.370851
		H72	0.406974
NTO^-	-0.72742	Mg	1.126548

From the analysis, the total atomic charges of NTO^- is not exactly equal with 1 which dues to the extensive hydrogen bonds in the molecule and the weak bonds between Mg and NTO anion. The charge of Mg atom is 1.126 548 e, which is in accord with the covalent bonds between Mg and oxygen atoms of the water molecules in the population analysis and the crystal structure solution. The charges on nitrogen atoms of the NTO ring appear to be negative while the nitrogen atom N4 on the nitro group ($—NO_2$) appears to be positive, so $—NO_2$ will lost first when the compound is heated to some uniform temperature and this result is in agreement with that of the thermal decomposition experiment. All the carbon atoms and hydrogen atoms on the NTO anion are assigned positive charges. The total atomic charges of the coordinate waters are 0.045 838 e (O4 H41 H42), 0.046 661 e (O5 H51 H52) and 0.074 224 e (O6 H61 H62), which indicate that 0.045 838 e, 0.046 661 e and 0.074 224 e deviate from H_2O to Mg to form the coordinate bonds.

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Preliminary Study on Environment-friendly Colored Smoke

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Abstract: Formulations of colored smoke were studied, in which a series of new environment-friendly dyes were used. Experiment results showed that potassium chlorate ($KClO_3$) and lactose ($C_{12}H_{22}O_{11}$) are the best oxidizer and the fuel, and 50% red, yellow or blue dye is the optimum content in the primary color formulations. In the synthesis of color 66.6% red and 33.3% blue, 50% red and 50% yellow, 33.3% blue and 66.6% yellow are the optimums to synthesize purple, orange and green respectively. The non-toxicity dyes used in the study were preliminarily verified through biological experiment.

Key words: applied chemistry; colored smoke composition; environment-friendly; dye; color synthesizing

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[$Mg(H_2O)_6$]$(NTO)_2 \cdot 2H_2O$的热分解机理及量子化学研究

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摘要: 用碱式碳酸镁与3-硝基-1,2,4-三唑-5-酮(NTO)在水中合成了[$Mg(H_2O)_6$]$(NTO)_2 \cdot 2H_2O$。用DSC, TG/DTG和IR研究了它的热分解机理。以晶体实验构型为初始值对配合物用6-31G基组在B3LYP水平下进行量子化学计算。结果表明Mg原子与配位水分子之间的配位键具有共价键性质。NTO环上的成环氮原子都带负电荷,而硝基上(—NO_2)的氮原子带有正电荷,说明标题配合物在加热至一定温度时,—NO_2将首先离去,这与热分解实验结果一致。

关键词: 物理化学; 3-硝基-1,2,4-三唑-5-酮(NTO); 镁配合物; 热分解机理; 量子化学研究
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