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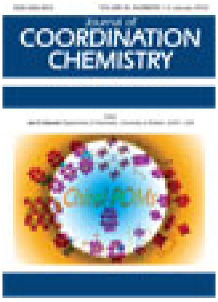

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Synthesis, crystal structure, thermal decomposition, and non-isothermal reaction kinetic analysis of an energetic complex: $[Mg(CHZ)_3](ClO_4)_2$ (CHZ=carbohydrazide)

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Synthesis, crystal structure, thermal decomposition, and non-isothermal reaction kinetic analysis of an energetic complex: $[Mg(CHZ)_3](ClO_4)_2$ (CHZ = carbohydrazide)

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An energetic complex $[Mg(CHZ)_3](ClO_4)_2$ was synthesized by the reaction of carbohydrazide (CHZ) with magnesium perchlorate. The product was characterized by X-ray single-crystal diffraction, elemental analysis, and IR spectroscopy. The crystal belongs to the monoclinic system with space group *P2(1)/n*. Cell parameters: $a = 10.034(2)$ Å, $b = 8.5069(16)$ Å, $c = 21.285(4)$ Å, $\beta = 100.901(3)^\circ$, $V = 1784.1(6)$ Å^3, $Z = 4$. The central magnesium is six-coordinate with three oxygen atoms of carbonyl groups and three terminal nitrogen atoms of the hydrazine groups from three CHZs to form a distorted octahedron. Differential scanning calorimetry and thermogravimetric-differential thermogravimetric analysis were applied to assess the thermal decomposition behavior. The kinetic parameters were obtained by non-isothermal reaction kinetics. The equation can be expressed as $\frac{d\alpha}{dT} = 4 \times 10^{6.13}\alpha^{3/4}e^{8.51\times10^3/T}$. Moreover, the values of critical temperature of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$, and the energy of combustion were obtained as 284°C, $-169.76\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $65.46\,\mathrm{kJ\,mol^{-1}}$, $154.27\,\mathrm{kJ\,mol^{-1}}$, and $6759\,\mathrm{kJkg^{-1}}$, respectively.

Keywords: Magnesium; Carbohydrazide; Energetic complex; Crystal structure; Thermal analysis

1. Introduction

Primary explosives that are used in small quantities to generate a detonation wave when subjected to a flame, heat, impact, electric spark or friction have been widely used in military and civilian areas [1–3]. Long-term use of mercury fulminate, lead azide, and lead styphnate as primary explosives has resulted in serious environmental contamination, and become a major health hazard for both military and civilian personnel [4–6]. To develop environmentally-friendly primary explosives with excellent performance, interests focus on energetic coordination compounds. Due to the positive heat of formation and thermal stability, nitrogen heterocyclic rings have obtained attention as ligands to construct energetic coordination compounds, such as 5-nitrotetrazole [2, 4, 7–9], 1,5-diaminotetrazole [10–14], and 3-azido-1,2,4-triazole [15–18]. On the other side,

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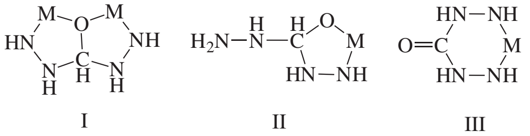

Scheme 1. Coordination models of CHZ.

carbohydrazide (CHZ) and hydrazine are interesting azotic chain ligands with several lone-pair electrons [3, 19–24].

CHZ is a hydrazine, which has more functional groups. As an azotic ligand with lone electron pairs, CHZ may coordinate with many metal ions monodentate or multidentate [25]. Three coordination models are shown in scheme 1. As a tridentate ligand, CHZ coordinates with two central cations *via* two terminal nitrogen atoms and the carbonyl oxygen. Each CHZ can form two five-member chelate rings with two metal ions sharing C–O. In $\{[Ca(CHZ)_2(H_2O)](NTO)_2 \cdot 3.5H_2O\}_n$, $\{[Sr(CHZ)_2(H_2O)] \cdot (NTO)_2 \cdot 3.5H_2O\}_n$, $[Sr(CHZ)(TNR)(H_2O)(OH)]_2 \cdot 2H_2O$, $[Mn_2(TNR)_2(CHZ)_2(H_2O)_4] \cdot 2H_2O$, and $Mn_2(CHZ)_2(H_2O)_2(SO_4)_2$, coordination model I of CHZ was authenticated by Zhang and co-workers [26–29]. The most common coordination model of CHZ is II. Sinditskii *et al.* [30] and Zhang *et al.* [21, 31–33] investigated molecular and crystal structures of metal CHZ perchlorates using X-ray single-crystal diffraction, reporting that CHZ coordinates through carbonyl and amine, forming a five-membered ring. This model was also confirmed in some complexes of trinitromethane [22, 23] and azide [34]. However, in 2004, Talawar *et al.* [3] characterized the molecular structures of Co, Ni, Zn, and Cu complexes of CHZ perchlorate by metal content analysis, infrared (IR) spectra, and electron spectroscopy, suggesting that CHZ coordinates through both end amino nitrogen atoms, forming a six-membered ring. Huang *et al.* [35, 36] studied the geometry, electronic structure, IR spectra, and thermochemical properties of transition metal CHZ perchlorates with two coordination models by applying density functional theory. In Co, Ni, and Cu complexes of CHZ perchlorate with both end amines coordinating, the results show that all three complexes have six-coordinate octahedra; both perchlorates also coordinate with the copper.

Energetic materials based on alkaline-earth metals have aroused interest. In 2009, Klapötke reported the synthesis, characterization, and energetic properties of alkaline earth metal salts of 5-nitro-2H-tetrazole, indicating future use as energetic compounds. In addition, Klapötke synthesized and structurally investigated strontium and barium salts of tetrazole-5-carboxylic acid; their properties make them ecologically interesting substitutes for toxic pyrotechnic compositions [37, 38].

Metal complexes based on CHZ perchlorate exhibit excellent energetic properties and thermal stability. Zinc and cadmium CHZ perchlorates are widely used as lead-free primary explosives in industrial detonators [21, 33, 39, 40]. However, most of these studies focus on transition metals. Reports on alkaline-earth metal CHZ perchlorates are rare. In 2009, Huang *et al.* [41] investigated the molecular geometries, electronic structures, and stabilities of alkaline-earth metal CHZ perchlorates by applying the Heyd–Scuseria–Ernzerhof (HSE) screened hybrid density functional. He reported that Be and Mg complexes have six-coordinate octahedra, as previously reported for transition metal complexes, but Ca, Sr, and Ba complexes have additional coordinated oxygen atoms from perchlorate.

Herein, we synthesize an energetic coordination compound, investigate the crystal structure, thermal decomposition, non-isothermal kinetics, energy of combustion, and calculated the critical temperature of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$.

2. Experimental

Caution!

$[Mg(CHZ)_3](ClO_4)_2$ as an energetic complex tends to explode under certain stimulus such as heat, flame, friction and impact. When preparing it, appropriate safety precautions should be taken, especially on a large scale.

2.1. *General method*

Magnesium oxide and perchloric acid are analytically pure commercial products. CHZ is used as supplied by the industry. Elemental analysis was performed with a Flash EA 1112 fully-automatic trace element analyzer. Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recorded on a Bruker Equinox 55 infrared spectrometer using KBr pellets from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Sample (about 0.2 mg) was placed in aluminum pans in static air for differential scanning calorimetry (DSC) (CDR-4, Shanghai Precision & Scientific Instrument Co., Ltd) with various heating rates (5, 10, 15, 20°C · min^{-1}). Measurements of thermogravimetric analysis (TGA) (Pyris-1, Perkin-Elmer, USA) were performed at a heating rate of 10°C · min^{-1} in platinum sample pans (sample about 0.2 mg) using dry oxygen-free nitrogen with a flow rate of 20 mL min^{-1}.

2.2. *Bomb calorimetry*

Calorimetric measurements of $[Mg(CHZ)_3](ClO_4)_2$ were performed with a Parr-6200 bomb calorimeter (static jacket) equipped with a 6510 water handling system and a Parr-1104 high-strength bomb for the combustion of energetic materials. The calorimeter was calibrated by the combustion of certified benzoic acid (about 1.0 g, pellet) in an oxygen atmosphere at a pressure of 3.10 MPa. Samples of $[Mg(CHZ)_3](ClO_4)_2$ (about 0.5 g) were prepared and placed in combustion pots, which were subsequently burned in a 3.10 MPa atmosphere of pure oxygen.

2.3. *Synthesis of $[Mg(CHZ)_3](ClO_4)_2$*

0.4 g MgO (0.01 mol) was added slowly to a solution of perchloric acid (1.6 mL, 0.02 mol, w = 70–72%) in 10 mL deionized water at room temperature, under stirring. The magnesium perchlorate solution was obtained after adequate reaction. CHZ (2.7 g, 0.03 mol) was dissolved in 20 mL of deionized water and heated to 70°C. The magnesium perchlorate was added gradually dropwise under stirring. The mixture was stirred at 70°C for 30 min and then naturally cooled to room temperature. The product was collected by filtration, washed with deionized water and alcohol, and dried in a vacuum dryer. Single crystals of $[Mg(CHZ)_3](ClO_4)_2$ suitable for X-ray analyses were obtained by slow crystallization from the filtrate for 15 days. Anal. Calcd for

Table 1. Crystallographic data and structure determination details for $[Mg(CHZ)_3](ClO_4)_2$.

Empirical formula	$C_3H_{18}Cl_2MgN_{12}O_{11}$
Formula weight $(g \cdot mol^{-1})$	493.50
Temperature (K)	133(2)
Crystal system	Monoclinic
Space group	*P2(1)/n*
Unit cell dimensions (Å, °)	
a	10.034(2)
b	8.5069(16)
c	21.285(4)
β	100.901(3)
Volume ($Å^3$), *Z*	1784.1(6), 4
Calculated density ($g\ cm^{-3}$)	1.837
Absorption coefficient (mm^{-1})	0.484
Crystal dim. (mm)	0.40 × 0.38 × 0.16
θ range for data collection (°)	2.39–29.12
Limiting indices	$-13 \leq h \leq 12$; $-11 \leq k \leq 11$; $-26 \leq l \leq 29$
Reflections collected	15,117
Independent reflections (R_{int})	4764 (0.0307)
Data/restraints/parameters	4764/7/362
Goodness-of-fit on F^2	0.999
Final R_1, wR_2 $[I > 2\sigma(I)]^a$	0.0471, 0.1074
R_1, wR_2 indices (all data)^a	0.0531, 0.1121
Largest difference peak and hole ($e\ Å^{-3}$)	0.831 and −0.877

$^a w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 2.6600P]$, where $P = (F_o^2 + 2F_c^2)/3$.

$[Mg(CHZ)_3](ClO_4)_2$ (%): C, 7.29; H, 3.65; N, 34.04. Found (%): C, 7.25; H, 3.66; N, 34.12. FT-IR (KBr pellet) data (ν cm^{-1}): 3363 (ν_{asN-H}), 3317 (ν_{sN-H}), 1658 ($\nu_{C=O}$), 1548 (δ_{N-H}), 1080 (ν_{ClO4-}), 626 (ν_{ClO4-}).

2.4. *X-ray crystallography*

A colorless chunk crystal of $[Mg(CHZ)_3](ClO_4)_2$, 0.40 mm × 0.38 mm × 0.16 mm obtained as above was used in the X-ray diffraction study. Data collections were performed on a Rigaku AFC-10/Saturn 724^+ CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 93(2) K using the multi-scan mode. The structure of $[Mg(CHZ)_3](ClO_4)_2$ was solved by direct methods using SHELXS-97 [42, 43] and refined by full-matrix least-squares procedures on F^2 with SHELXL-97 [44]. All non-hydrogen atoms were obtained from the difference Fourier map and refined anisotropically. Hydrogen atoms were generated geometrically, assigned appropriated isotropic thermal parameters, and included in structure factor calculations. Crystallographic data and experimental details for structure analyses are summarized in table 1.

3. Results and discussion

3.1. *Structural description of $[Mg(CHZ)_3](ClO_4)_2$*

The $[Mg(CHZ)_3](ClO_4)_2$ crystal belongs to the monoclinic system with space group *P2(1)/n*. Structure analysis shows that the asymmetric unit is comprised of one central

Table 2. Selected bond lengths (Å) and angles (°) for $[Mg(CHZ)_3](ClO_4)_2$.

Mg1–O3	2.0107(16)	O2–C2	1.261(2)	N6–C2	1.348(3)
Mg1–O2	2.0256(16)	O3–C3	1.255(2)	N7–C2	1.331(3)
Mg1–O1	2.0475(16)	N1–N2	1.415(2)	N7–N8	1.413(3)
Mg1–N1	2.229(2)	N2–C1	1.343(3)	N9–N10	1.415(2)
Mg1–N5	2.2309(19)	N3–C1	1.336(3)	N10–C3	1.347(3)
Mg1–N9	2.238(2)	N3–N4	1.405(2)	N11–C3	1.332(3)
O1–C1	1.264(2)	N5–N6	1.415(3)	N11–N12	1.404(3)
O3–Mg1–O2	94.81(7)	O1–Mg1–N5	167.08(7)	C2–O2–Mg1	117.04(13)
O3–Mg1–O1	91.35(6)	N1–Mg1–N5	100.50(7)	C3–O3–Mg1	118.09(13)
O2–Mg1–O1	91.08(7)	O3–Mg1–N9	76.71(6)	N2–N1–Mg1	107.73(12)
O3–Mg1–N1	161.61(7)	O2–Mg1–N9	163.58(7)	N6–N5–Mg1	106.02(12)
O2–Mg1–N1	99.04(7)	O1–Mg1–N9	103.01(7)	N10–N9–Mg1	106.49(12)
O1–Mg1–N1	76.42(6)	N1–Mg1–N9	92.51(7)	O1–C1–N2	121.28(18)
O3–Mg1–N5	94.36(7)	N5–Mg1–N9	89.60(7)	C1–N2–N1	116.73(17)
O2–Mg1–N5	76.91(7)	C1–O1–Mg1	117.26(13)		

Mg(II), three CHZs, and two perchlorates. The structure of $[Mg(CHZ)_3](ClO_4)_2$ is similar to the reported transition metal complexes of CHZ perchlorates [45–48]. Selected bond lengths and angles for $[Mg(CHZ)_3](ClO_4)_2$ are listed in table 2.

The central magnesium is six-coordinate with three oxygen atoms of carbonyl groups and three terminal nitrogen atoms of hydrazine from three different CHZs, which form a $[MgN_3O_3]$ polyhedron (figure 1). The bond lengths of magnesium and three nitrogen atoms are 2.229(2), 2.2309(19), and 2.238(2) Å, with an average of 2.2327 Å. The Mg–O bond lengths are 2.0475(16), 2.0256(16), and 2.0107(16) Å. All these bond lengths are typical for coordination bonds. Huang *et al.* [41] investigated the geometry of $[Mg(CHZ)_3](ClO_4)_2$ using the HSE screened hybrid density functional. He reported bond lengths of Mg–O and Mg–N as 2.0 and 2.2–2.3 Å, respectively, which correspond to the experimental results. The trans bond angles, O1–Mg1–N5 of 167.08(7)°, O2–Mg1–N9 of 163.58(7)°, and O3–Mg1–N1 of 161.61(7)°, deviate from ideal value of 180°. Therefore, the coordination geometry around Mg(II) ion is a considerable distorted octahedron.

In $[Mg(CHZ)_3](ClO_4)_2$, CHZ exhibits typical bidentate coordination. As a bidentate ligand, CHZ is coordinated with Mg(II) ion through the carbonyl oxygen and a terminal nitrogen, corresponding to the result given by Huang's theoretical study [41]. CHZ also has this coordination in transition metal complexes of CHZ perchlorate [21, 31–33]. However, in other alkaline earth metal complexes, CHZ is always tridentate, as in Zhang's reported complexes, $\{[Ca(CHZ)_2(H_2O)](NTO)_2 \cdot 3.5H_2O\}_n$ [49], $\{[Sr(CHZ)_2(H_2O)] \cdot (NTO)_2 \cdot 3.5H_2O\}_n$ [27], and $[Sr(CHZ)(TNR)(H_2O)(OH)]_2 \cdot 2H_2O$ [26]. This may be attributed to the smaller ionic radius of Mg(II), which gives less room for the CHZ to coordinate. Also, in the alkaline earth metals, Mg with smaller atomic radius has stronger coordination ability than Sr, Ca, and Ba. So, CHZ exhibits the relative weaker coordinate ability, and results in the bidentate coordination.

Three five-member planar chelate rings were formed by one Mg(II) and three CHZs, resulting in minimum steric hindrance. Figure 2 displays the planar structure of the chelate rings in $[Mg(CHZ)_3](ClO_4)_2$. Equations of the planes are: A, $6.213x + 6.671y - 1.649z = 5.7074$ (mean deviation, 0.0234 Å) for [Mg1, C1, O1, N1, N2]; B, $-0.72x + 2.349y + 20.321z = 13.8572$ (mean deviation, 0.0641 Å) for [Mg1, C2, O2, N5, N6]; C, $-5.665x + 6.72y - 2.726z = 0.3371$ (mean deviation, 0.042 Å) for [Mg1, C3, O3, N9, N10]. The angle between the planes A and B is 77.8°, A and C is 74.9°, B and C

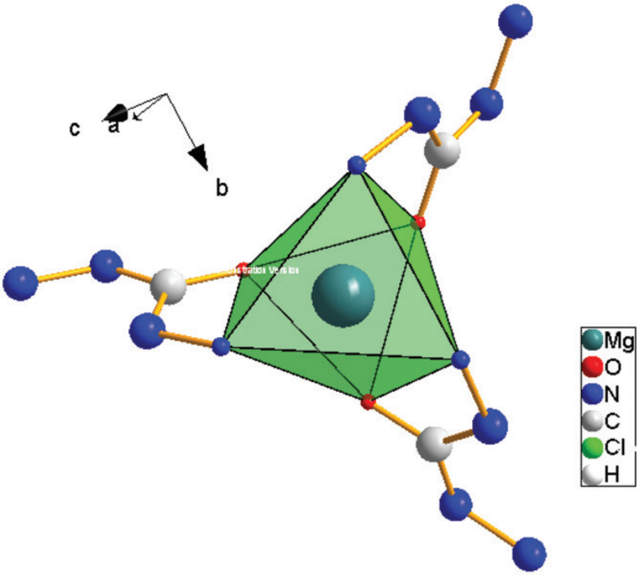

Figure 1. Distorted octahedron of central magnesium coordinated by three CHZ molecules.

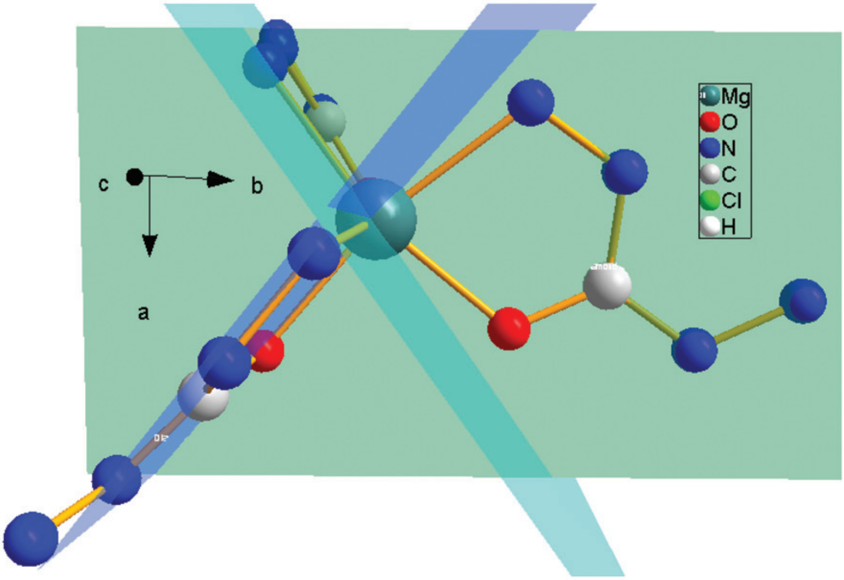

Figure 2. Planes formed by five-member chelate rings in $[Mg(CHZ)_3](ClO_4)_2$.

is 88.3°. The uncoordinated hydrazine groups are in a semi-dissociated state. This semi-dissociated structure leads to good molecule flexibility to the title complex.

As shown in the packing diagram of $[Mg(CHZ)_3](ClO_4)_2$ (figure 3), many hydrogen bonds between N and O were formed to link molecules into a 3-D network. Table 3 summarizes the hydrogen bond parameters. When constructing the stable architecture,

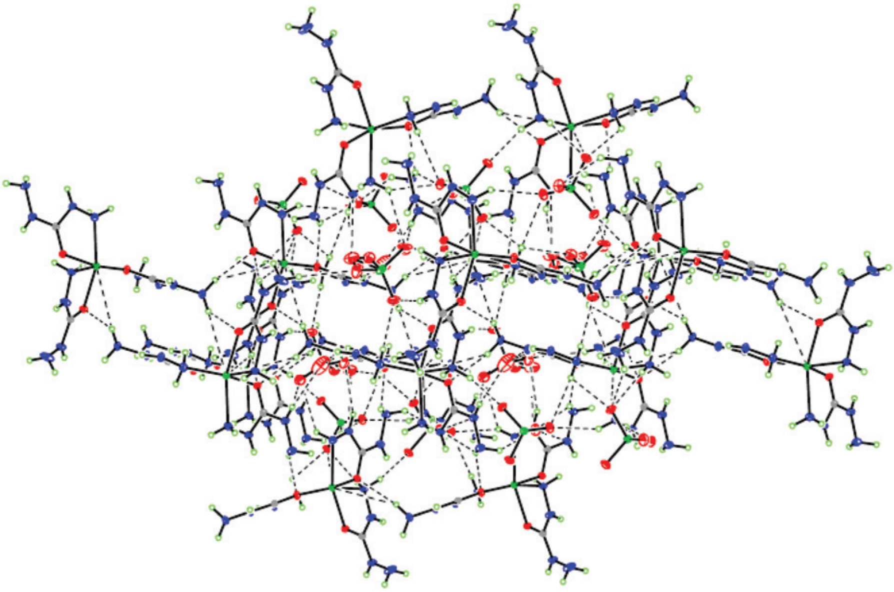

Figure 3. Packing diagram of $[Mg(CHZ)_3](ClO_4)_2$ in crystal viewed along the *a*-axis.

Table 3. Hydrogen bond lengths (Å) and angles (°) for $[Mg(CHZ)_3](ClO_4)_2$.

D–H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	Angle (D–H···A)
N1–H1···O5#1	0.90	2.13	3.0296	178
N4–H4···O7#2	0.88	2.44	3.0951	131
N4–H4···O2#3	0.83	2.34	3.0084	138
N7–H7···O11#4	0.90	2.16	3.0628	177
N9–H9···O6#5	0.91	2.29	3.0696	144
N10–H10···O8	0.86	2.22	3.0269	157
N11–H11···O1#6	0.85	2.12	2.9695	172

Symmetry transformations used to generate equivalent atoms for $[Mg(CHZ)_3](ClO_4)_2$, #1: $1/2-x$, $-1/2+y$, $3/2-z$; #2: $3/2-x$, $-1/2+y$, $3/2-z$; #3: $3/2-x$, $1/2+y$, $3/2-z$; #4: $1+x$, $1+y$, z; #5: $1/2-x$, $1/2+y$, $3/2-z$; #6: $1-x$, $1-y$, $1-z$.

ClO_4^- plays an important role to connect various coordinated cations *via* hydrogen bonds, such as N1–H1···O5#1, N9–H9···O6#5, N4–H4···O7#2, and N10–H10···O8. In addition, hydrogen bonds are also found between CHZ molecules. Except for the hydrogen bonding interaction, the electrostatic forces also make an important contribution to the stability of the coordination compound.

3.2. *Thermal decomposition*

To assess the thermal behavior of $[Mg(CHZ)_3](ClO_4)_2$, thermal decomposition processes were investigated by using DSC and TGA measurements. The DSC and thermogravimetric-differential thermogravimetric (TG-DTG) curves under linear heating rate of 10°C min^{-1} are shown in figures 4 and 5. The tested sample is a

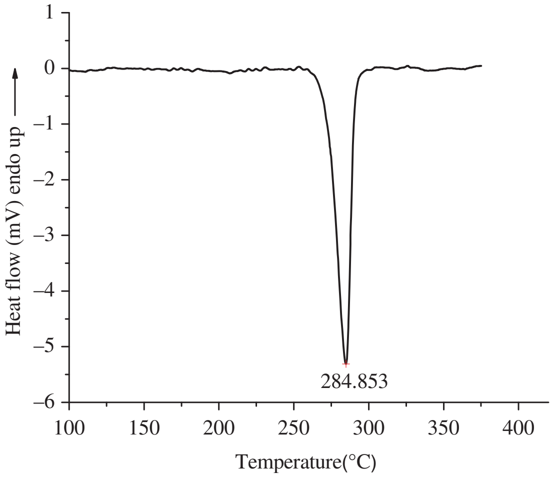

Figure 4. DSC curve of $[Mg(CHZ)_3](ClO_4)_2$ at 10°C min^{-1}.

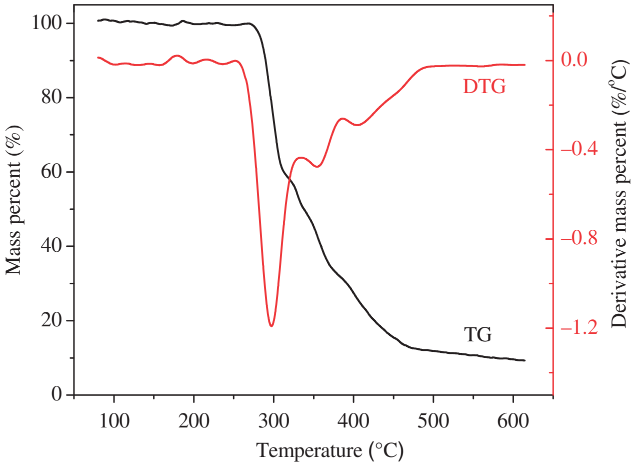

Figure 5. TG-DTG curves of $[Mg(CHZ)_3](ClO_4)_2$ at 10°C min^{-1}.

crystalline solid, which was dried in a water bath oven at 50°C to remove any moisture beside crystal and hydrated water.

In the DSC curve, there is only one sharp exothermic decomposition at 257–298°C, with the peak temperature of 285°C. Contrasting with Cu and Fe complexes of CHZ perchlorate, $[Mg(CHZ)_3](ClO_4)_2$ is more thermally stable with higher onset temperature of 257°C, where the others are 120°C and 152.7°C, respectively. Different from endothermal melting of some transition metal CHZ perchlorates, the whole thermal decomposition process of $[Mg(CHZ)_3](ClO_4)_2$ is exothermal [45–48]. Corresponding to the exothermic decomposition, mass loss was found in TG-DTG curves. A great amount of heat and gases were released in the decomposition. The final residue is white loose powder with light mass, probably MgO. The mass is 9.5% of the initial mass, coincident with the calculated value of MgO, 8.2%. The absorption band of the residue at 600°C also proves that the final residue is MgO.

3.3. *Non-isothermal reaction kinetic analysis*

The Kissinger's [50] method and Ozawa–Doyle's [51] method are used to determine the apparent activation energy (E_a/kJ mol^{-1}) and the pre-exponential factor (A/s^{-1}) of the exothermic decomposition of $[\mathrm{Mg(CHZ)_3}](\mathrm{ClO_4})_2$ from the multiple non-isothermal DSC curves obtained with different rates of heating. The two equations can be described as follows:

$$\frac{\mathrm{d}\ln(\beta/T_{\mathrm{p}}^2)}{\mathrm{d}(1/T_{\mathrm{p}})} = -\frac{E_{\mathrm{a}}}{R} \quad (\textit{Kissinger's})$$

$$\lg\beta + \frac{0.4567E_{\mathrm{a}}}{RT_{\mathrm{p}}} = C \quad (\textit{Ozawa}-\textit{Doyle's})$$

where T_{p} is the peak temperature, °C; R is the gas constant, 8.314 J mol^{-1} K^{-1}; β is the linear heating rate, °C min^{-1}; C is a constant. The peak temperature (266, 285, 296, and 313°C) in the non-isothermal DSC curves corresponds to the same conversion degrees at various heating rates (5, 10, 15, and 20°C min^{-1}). The values of E_a were obtained by the slope of the fitted regression lines of $\ln(\beta/T_{\mathrm{p}}^2)$ or $\lg\beta$ *versus* $1/T_{\mathrm{p}}$.

Four integral equations [Ordinary–integral (1), MacCallum–Tanner (2), Satava–Sestak (3), Agrawal (4)] are employed to obtain the values of E_a, A and the most probable kinetic model function from a single non-isothermal DSC curve at a heat rate of 10°C min^{-1}, where T is the temperature, α is the conversion degree, $G(\alpha)$ and $f(\alpha)$ are the integral and differential model function.

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{1}$$

$$\lg[G(\alpha)] = \lg\left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4357} - \frac{0.449+0.217E}{0.001}\frac{1}{T} \tag{2}$$

$$\lg G(\alpha) = \lg\frac{AE}{R\beta} - 2.315 - 0.4567\frac{E}{RT} \tag{3}$$

$$\ln\left[\frac{GR}{T^2}\right] = \ln\left\{\frac{AR}{\beta E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-5\frac{RT^2}{E}}\right]\right\} - \frac{E}{RT} \tag{4}$$

The relationship of conversion degrees *versus* temperature was obtained through mathematic means and is shown in figure 6. Forty-one types of kinetic model functions and the basic data obtained by DSC curve were put into the four equations for calculation [52, 53].

The data of E, $\lg A$, linear correlation coefficient (R), and standard mean square deviation (Q) were calculated with the linear least-squares method. The most probable mechanism function is selected by the better values of R, Q, and approximate values of E and $\lg A$ with Kissinger and Ozawa–Doyle methods. The kinetic parameters are listed in table 4. Calculated results using various methods are similar and in the normal range of kinetic parameters for the thermal decomposition of solid materials [54]. Therefore, we conclude that the exothermic decomposition process is according to the Mampel Power law, with the value of n is 1/4. The mechanism function $G(\alpha) = \alpha^{1/4}$ and

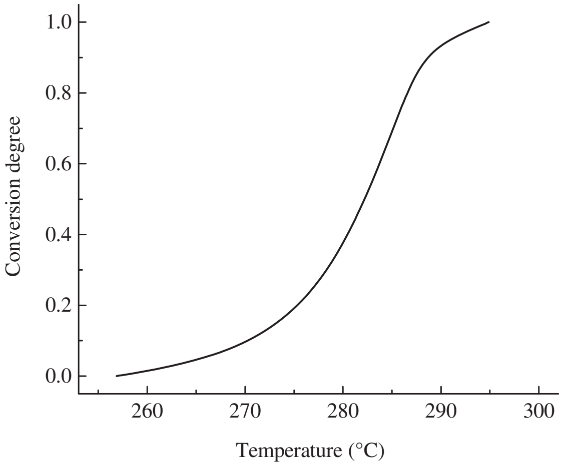

Figure 6. Dependence of conversion degree on temperature of the exothermic decomposition process of $[Mg(CHZ)_3](ClO_4)_2$.

Table 4. Kinetic parameters for the exothermic decomposition of $[Mg(CHZ)_3](ClO_4)_2$.

Method	E_a (kJ mol^{-1})	lg(A/s^{-1})	R	Q
Ordinary–integral	69.16	7.70	−0.9974	0.0102
MacCallum–Tanner	70.27	4.24	−0.9980	0.0044
Satava–Sestak	74.52	4.88	−0.9980	0.0044
Agrawal	69.16	7.69	−0.9974	0.0102
Mean	70.78	6.13		
Kissinger	69.81	4.17	−0.9853	0.1112
Ozawa–Doyle	75.26		−0.9887	0.0478

$f(\alpha) = 4\alpha^{3/4}$. Substituting $f(\alpha)$ with $4\alpha^{3/4}$, E_a with 70.78 kJ mol^{-1}, and lg(A/s^{-1}) with 6.13 into equation

$$\frac{d\alpha}{dT} = Af(\alpha)e^{-E/RT}$$

the kinetic equation may be described as

$$\frac{d\alpha}{dT} = 4 \times 10^{6.13}\alpha^{3/4}e^{8.51\times10^3/T}$$

3.4. *Calculation of critical temperature of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$*

The value of the peak temperature corresponding to $\beta \rightarrow 0$ obtained according to the following equation [55] is 250°C, where b and c are coefficients.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2$$

The corresponding critical temperatures of thermal explosion (T_{bp}) obtained is 284°C, where R is the gas constant, E_O is the value of E_{a} by Ozawa's method.

$$T_{\mathrm{bp}} = \frac{E_O - \sqrt{E_O^2 - 4E_O R T_{\mathrm{p0}}}}{2R}$$

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) of the decomposition reaction of $[\mathrm{Mg(CHZ)_3}](\mathrm{ClO_4})_2$ corresponding to $T = T_{\mathrm{p0}}$, $E_{\mathrm{a}} = E_{\mathrm{K}}$, and $A = A_{\mathrm{K}}$ (obtained by Kissinger's method), obtained by the following equations [52] are $-169.76\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $65.46\,\mathrm{kJ\,mol^{-1}}$, and $154.27\,\mathrm{kJ\,mol^{-1}}$, respectively.

$$A = \frac{k_{\mathrm{B}} T}{h} e^{\Delta S^{\neq}/R}$$
$$\Delta H^{\neq} = E_{\mathrm{a}} - RT$$
$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

where k_{B} is the Boltzmann constant (1.3807×10^{-23} J K^{-1}) and h is the Planck constant (6.626×10^{-34} J s^{-1}).

3.5. *Energy of combustion*

Energy of combustion and formation are significant characteristics to assess the energetic properties of a new compound. The constant volume energy of combustion [$\Delta_{\mathrm{c}} U_{\mathrm{v}}$ (kJ kg^{-1})] of $[\mathrm{Mg(CHZ)_3}](\mathrm{ClO_4})_2$ was measured by applying the bomb calorimeter with 6759 kJkg^{-1}. The constant pressure energy of combustion [$\Delta_{\mathrm{c}} U_{\mathrm{p}}$ (6778 kJkg^{-1})] was given by a correction for change in gas volume during combustion, equation (7). Then the standard energy of formation [$\Delta_{\mathrm{f}} H^o$ (−1037 kJmol^{-1})] for $[\mathrm{Mg(CHZ)_3}](\mathrm{ClO_4})_2$ was back-calculated from standard enthalpy of combustion on the basis of the general combustion equation, equation (5), Hess's Law as applied in equation (6), incorporating the known standard heats of formation for water (−285.83 kJmol^{-1}), carbon dioxide (−393.51 kJmol^{-1}), and magnesium oxide (−601.63 kJmol^{-1}).

$$\mathrm{C_3H_{18}Cl_2MgN_{12}O_{11}}(s) + 5/2\mathrm{O_2}(g) \rightarrow \mathrm{MgO}(s) + 3\mathrm{CO_2}(g) + 9\mathrm{H_2O}(l) + 6\mathrm{N_2} + \mathrm{Cl_2} \tag{5}$$

$$\begin{aligned}\Delta_{\mathrm{f}}\mathrm{H}^o_{\mathrm{m}}[\mathrm{C_3H_{18}Cl_2MgN_{12}O_{11}}(s)] = {}& \Delta_{\mathrm{f}}\mathrm{H}^o_{\mathrm{m}}[\mathrm{MgO}(s)] + 3\Delta_{\mathrm{f}}\mathrm{H}^o_{\mathrm{m}}[\mathrm{CO_2}(g)] + 9\Delta_{\mathrm{f}}\mathrm{H}^o_{\mathrm{m}}[\mathrm{H_2O}(l)] \\ & - \Delta_{\mathrm{c}}\mathrm{H}^o_{\mathrm{m}}[\mathrm{C_3H_{18}Cl_2MgN_{12}O_{11}}(s)]\end{aligned} \tag{6}$$

$$\Delta_{\mathrm{c}} U_{\mathrm{p}} = \Delta_{\mathrm{c}} U_{\mathrm{v}} + \Delta n_{\mathrm{g}} RT \tag{7}$$

The $\Delta_{\mathrm{c}} U_{\mathrm{v}}$ of $[\mathrm{Mg(CHZ)_3}](\mathrm{ClO_4})_2$ is 853 kJkg^{-1} higher than that of $\mathrm{Zn(CHZ)_3(ClO_4)_2}$ (5906 kJkg^{-1}) [46] and by 773 kJkg^{-1} lower than that of magnesium tetrazole-1-acetic acid (7532 kJkg^{-1}) [56]. The energies of combustion of cyclotrimethylenetrinitramine (RDX) [57] and cyclotetramethylenetetranitramine (HMX) reported in the literature are 9600 and 9440–9880 kJkg^{-1}, respectively, both higher than that of $[\mathrm{Mg(CHZ)_3}](\mathrm{ClO_4})_2$.

4. Conclusion

Reacting CHZ with magnesium perchlorate, we obtained an energetic coordination compound $[Mg(CHZ)_3](ClO_4)_2$. In $[Mg(CHZ)_3](ClO_4)_2$, magnesium is six-coordinate with a distorted octahedral configuration by three oxygen atoms of the carbonyl groups and three terminal nitrogen atoms of the hydrazine. The decomposition of $[Mg(CHZ)_3](ClO_4)_2$ starts at 257°C with a great amount of heat and gases. The kinetic parameters of the primary exothermal process of $[Mg(CHZ)_3](ClO_4)_2$ were obtained by non-isothermal reaction kinetic analyses with one differential method and five integral methods. The kinetic equation is described as $\frac{d\alpha}{dT} = 4 \times 10^{6.13}\alpha^{3/4}e^{8.51\times10^3/T}$. The values of critical temperature of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ are 284°C, $-169.76\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $65.46\,\mathrm{kJ\,mol^{-1}}$, and $154.27\,\mathrm{kJ\,mol^{-1}}$, respectively. The constant volume energies of the combustion of $[Mg(CHZ)_3](ClO_4)_2$ was determined experimentally with the data of $6759\,\mathrm{kJkg^{-1}}$, and the energy of formation was calculated as $-1037\,\mathrm{kJmol^{-1}}$.

Supplementary material

CCDC 825402 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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