

# Synthesis, structure analysis and thermodynamics of $[\text{Ni}(\text{H}_2\text{O})_4(\text{TO})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (TO = 1,2,4-triazole-5-one)

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Received: 14 May 2009 / Accepted: 29 July 2009 / Published online: 28 August 2009  
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**Abstract** A novel complex  $[\text{Ni}(\text{H}_2\text{O})_4(\text{TO})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (TO = 1,2,4-triazole-5-one) was synthesized and structurally characterized by X-ray crystal diffraction analysis. The decomposition reaction kinetic of the complex was studied using TG-DTG. A multiple heating rate method was utilized to determine the apparent activation energy ( $E_a$ ) and pre-exponential constant ( $A$ ) of the former two decomposition stages, and the values are  $109.2 \text{ kJ mol}^{-1}$ ,  $10^{13.80} \text{ s}^{-1}$ ;  $108.0 \text{ kJ mol}^{-1}$ ,  $10^{23.23} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion, the entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and the free energy of activation ( $\Delta G^\ddagger$ ) of the initial two decomposition stages of the complex were also calculated. The standard enthalpy of formation of the new complex was determined as being  $-1464.55 \pm 1.70 \text{ kJ mol}^{-1}$  by a rotating-bomb calorimeter.

**Keywords** 1,2,4-Triazole-5-one · Nickel complex · Thermal analytical kinetic · Standard enthalpy of formation

## Introduction

Since 3-nitro-1,2,4-triazole-5-one (NTO) was first reported as a explosive agent in 1987 [1], metal complexes of 1,2,4-triazole derivatives [2, 3] used as ballistic modifiers have

intrigued worldwide interest in the field of energetic materials based on their high nitrogen composition, high enthalpies of formation and high densities. Until now, the syntheses, structures, explosive properties, thermodynamical and thermochemical properties of NTO metal salts have been extensively studied [4–7], while other metal complexes with simple 1,2,4-triazole derivatives were still in the stage of syntheses and characterization of their basic chemical properties [8–10]. Though many scientists have predicted the potential applications of metal complexes with TO as burning rate modifiers in the solid propellants [11–13], the metal complexes have not been extensively studied. In order to further explore thermodynamic properties of the transition metal complexes with TO, a new complex  $[\text{Ni}(\text{H}_2\text{O})_4(\text{TO})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  has been synthesized and characterized in this context. A multiple heating rate method was adopted to calculate the apparent activation energy ( $E_a$ ) and pre-exponential constant ( $A$ ) of the former two decomposition stages. And the standard enthalpy of formation of the new complex was determined by a precise rotating-bomb calorimeter.

## Experimental

### Materials

According to the literature method, formic acid (88%, Xi'an Chemical Co) and semicarbazide hydrochloride (99%, ACROS) were used to synthesize 1,2,4-triazole-5-one (TO), and the m.p. is  $234.04 \text{ }^\circ\text{C}$ , which is consistent with literatures [14, 15].  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (AR) was commercially available without further purification.

An appropriate amount of TO (1 mmol, 0.085 g) dissolved in water (5 mL) was dropped into an ethanol

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solution (15 mL) of nickel nitrate (0.5 mmol, 0.149 g) at 60 °C. After being filtered, the filtrate was left at the room temperature to obtain the green single crystal for X-ray measurement. The green precipitates were washed with anhydrous alcohol for three times and dried at room temperature for further analysis (58% yield based on nickel nitrate). Anal. calcd. for  $\text{NiC}_4\text{H}_{18}\text{N}_8\text{O}_{14}$ : C, 10.42%; H, 3.94%; N, 24.31%; Ni, 12.73%; found: C, 10.15%; H, 4.08%; N, 24.79%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH}^-)$  3428  $\text{cm}^{-1}$ ,  $\nu(\text{C-H})$  2858  $\text{cm}^{-1}$ ,  $\nu(\text{C=O})$  1756  $\text{cm}^{-1}$ ,  $\nu(\text{NO}_3^-)$  1386  $\text{cm}^{-1}$ ,  $\delta(\text{NO}_3^-)$  819  $\text{cm}^{-1}$ ,  $\nu(\text{C=N})$  1568  $\text{cm}^{-1}$ ,  $\nu(\text{C-N})$  1239  $\text{cm}^{-1}$ ,  $\delta$  (framework of triazolone) 962  $\text{cm}^{-1}$ , 746  $\text{cm}^{-1}$ , 521  $\text{cm}^{-1}$ .

### Instruments

C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer, IR spectrum was derived by a Nicolet 60 SXR FT-IR (Nicolet, USA) spectrometer in the 4000–400  $\text{cm}^{-1}$  regions (KBr pellets). The TG-DTG experiments were performed with a Netzsch STA 449C instrument with the heating rates of 5 °C  $\text{min}^{-1}$ , 10 °C  $\text{min}^{-1}$ , 15 °C  $\text{min}^{-1}$  and 20 °C  $\text{min}^{-1}$  in  $\text{N}_2$  flowing of 30  $\text{mL min}^{-1}$  and the sample mass is about 1.5 mg.

The constant-volume combustion energy of the complex was determined by a precise rotating bomb calorimeter (RBC-type II). The main experimental procedures were described previously [16]. The initial temperature was regulated to  $25.0000 \pm 0.0005$  °C, and the initial oxygen pressure was 2.5 MPa. The correct value of the heat exchange was calculated according to Linio–Pyfengdelel–Wsava formula [17]. The calorimeter was calibrated with benzoic acid of 99.999% purity. It had an isothermal heat of combustion at 25 °C of  $-26434 \pm 3$  J  $\text{g}^{-1}$ . The energy equivalent of calorimeter was determined to be  $17936.01 \pm 9.08$  kJ  $\text{K}^{-1}$ . The analytical methods of final products (gas, liquid and solid) were the same as these in reference [16]. The analytical results of the final products showed that the combustion reactions were complete. As a result, either carbon deposits or carbon monoxide formed during the combustion reactions and the amounts of  $\text{NO}_x$  in the final gas phase were negligible.

All single crystal X-ray experiments were performed on a Bruker Smart-1000CCD diffractometer with graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073$  Å) using  $\omega$  and  $\varphi$  scan modes within a range of  $2.45 < \theta < 25.09$  at 273 K. The crystal size was  $0.22 \times 0.18 \times 0.10$  mm. Of 2253 measures reflections, 1,526 observes reflections with  $I > 2\sigma(I)$  were used in the refinement. The single crystal structure of complex was solved by direct methods using SHELXS-97 [18] and all non-H atoms were located using subsequent Fourier-difference methods. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic ligands were generated geometrically. The

crystal data and structure refinement details for the complex are given in Table 1.

## Results and discussion

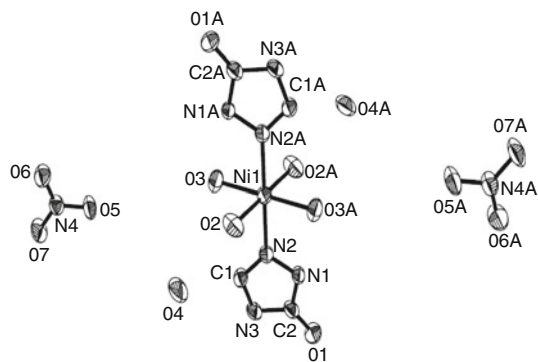
### Structure analysis

As shown in Fig. 1, the Ni(II) shows a typical octahedral central symmetrical geometry, where the Ni(II) coordinates with four oxygen atoms from coordinated water molecules in equatorial plane, and two axial nitrogen atoms from two TO ligands. Selected bond lengths and angles are shown in Table 2.

The hydrogen bonds of the complex have been examined by PLATON 98, and all the length and angles of hydrogen bonds fall in the normal range. The formation of the hydrogen bonds has significant effect on the density, stability of the complex. It was noteworthy that the formation of hydrogen bonds could decrease the shock sensitivity and increase the structural stability [2, 19, 20]. Hydrogen bonds formed with the oxygen atoms of  $\text{NO}_3^-$  contribute significantly to construct the three-dimensional network of the title complex. The electrostatic potential surface reveals that  $\text{NO}_3^-$  has an intrinsic hydrogen bonding topography in which there are six equivalent positions representing minimal energy for accepting  $\text{H}^+$ .

**Table 1** Crystallographic data for the complex

Empirical formula	$\text{C}_4\text{H}_{18}\text{N}_8\text{NiO}_{14}$
Formula weight	460.97
Space group	$P - 1$
$a/\text{nm}$	0.6636(2)
$b/\text{nm}$	0.8253(3)
$c/\text{nm}$	0.9219(5)
$\alpha/^\circ$	109.695(8)
$\beta/^\circ$	99.645(9)
$\gamma/^\circ$	106.634(6)
$V/\text{nm}^3$	0.4355(3)
$Z$	1
$D_c/\text{mg m}^{-3}$	1.758
$F(0\ 0\ 0)$	238
Absorption coefficient/ $\text{mm}^{-1}$	1.203
Limiting indices	$-7 \leq h \leq 7, -9 \leq k \leq 9,$ $-10 \leq l \leq 10$
Goodness-of-fit on $F^2$	0.907
$R(\text{int})$	0.0326
$R_1, wR_2 (I > 2\sigma(I))$	0.0506, 0.0989
$R_1, wR_2$ (all data)	0.0808, 0.1069
Largest diff. peak and hole/ $\text{e nm}^{-3}$	387, -482



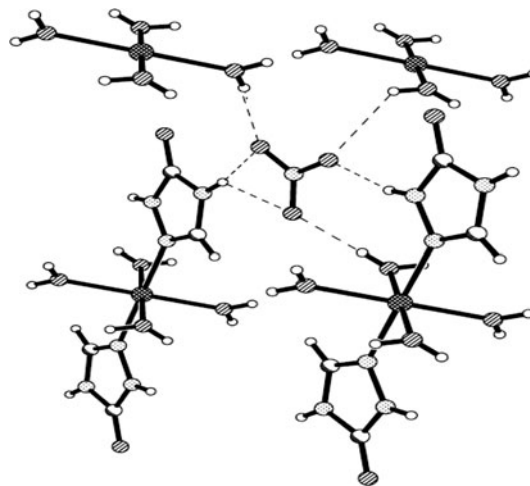
**Fig. 1** Coordination environment of Ni(II) in compound  $[\text{Ni}(\text{TO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

**Table 2** Selected bond lengths (nm) and bond angles ( $^\circ$ )

Ni(1)–O(2)	0.2021(3)	N(2)–C(1)	0.1286(5)
Ni(1)–O(3)	0.2052(3)	N(2)–N(1)	0.1379(5)
Ni(1)–N(2)	0.2080(4)	N(1)–C(2)	0.1346(5)
N(3)–C(1)	0.1347(5)	N(3)–C(2)	0.1369(6)
O(1)–C(2)	0.1236(5)		
O(2) <sup>1</sup> –Ni(1)–O(2)	180.0	N(2)–Ni(1)–N(2) <sup>1</sup>	180.00(18)
O(3) <sup>1</sup> –Ni(1)–O(3)	180.00(13)	C(1)–N(2)–N(1)	103.9(3)
O(2)–Ni(1)–O(3) <sup>i</sup>	90.18(15)	C(1)–N(2)–Ni(1)	131.5(3)
O(2)–Ni(1)–O(3)	89.82(15)	N(1)–N(2)–Ni(1)	124.6(3)
O(2) <sup>1</sup> –Ni(1)–N(2)	89.41(14)	C(2)–N(1)–N(2)	112.3(3)
O(2)–Ni(1)–N(2)	90.59(14)	C(1)–N(3)–C(2)	108.1(4)
O(3) <sup>i</sup> –Ni(1)–N(2)	91.69(14)	O(7)–N(4)–O(6)	122.4(4)
O(3)–Ni(1)–N(2)	88.31(14)	O(7)–N(4)–O(5)	119.4(4)
N(2)–C(1)–N(3)	112.3(4)	O(6)–N(4)–O(5)	118.2(4)
O(1)–C(2)–N(1)	128.7(4)	O(1)–C(2)–N(3)	127.9(4)
N(1)–C(2)–N(3)	103.3(4)		

The results indicate that the ideal  $\text{NO}_3^-$  would form six hydrogen bonds with the outside atoms. However, it is owing to the restriction of steric factors that such ideal mode is rare [21–23]. In the crystal structure of the title complex, the hydrogen bonds formed with oxygen atoms of  $\text{NO}_3^-$  express the ideal mode. Oxygen atoms of  $\text{NO}_3^-$  as the acceptor of the bifurcated hydrogen bonds form hydrogen bond with one oxygen atom and one nitrogen atoms, which are shown in Fig. 2. Hydrogen bond lengths and angles are listed in Table 3.

As shown in Fig. 3, the triazole rings are parallel with each other and the distance of the triazole between the layer are 3.1924, 3.3709 Å, respectively. Offset face-to-face  $\pi$ - $\pi$  stacking interactions involving triazole ring and hydrogen bonds construct the three-dimensional network of the complex  $[\text{Ni}(\text{H}_2\text{O})_4(\text{TO})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

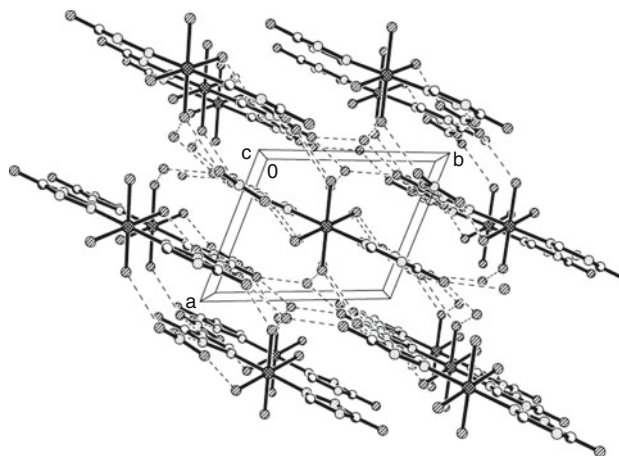


**Fig. 2** The hydrogen bonds formed with the oxygen atoms of  $\text{NO}_3^-$  (in order for clarity, the triazole rings coordinated with the  $\text{Ni}^{2+}$  in the top of the figure is omitted)

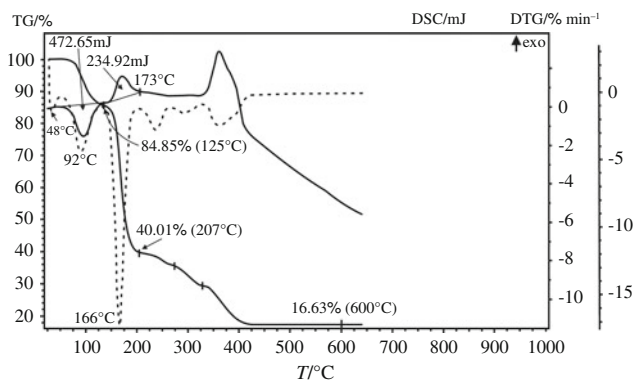
**Table 3** Hydrogen bond distance (nm) and angles ( $^\circ$ ) of the complex

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(2)–H(2A)···O(5) <sup>4</sup>	0.0876(10)	0.1926(17)	0.2787(5)	167(5)
N(3)–H(3)···O(5) <sup>3</sup>	0.086	0.194	0.2793(5)	170.1
O(3)–H(3B)···O(6) <sup>8</sup>	0.0878(10)	0.1889(14)	0.2760(5)	172(6)
N(3)–H(3)···O(6) <sup>3</sup>	0.086	0.246	0.3108(5)	132.9
N(1)–H(1)···O(7) <sup>2</sup>	0.086	0.197	0.2801(5)	161.1
O(3)–H(3A)···O(7) <sup>5</sup>	0.0877(10)	0.243(5)	0.3109(5)	135(6)
O(2)–H(2B)···O(4)	0.0878(10)	0.1817(16)	0.2684(5)	169(6)
O(3)–H(3A)···O(4) <sup>6</sup>	0.0877(10)	0.249(5)	0.3152(8)	133(5)
O(4)–H(4A)···O(1) <sup>7</sup>	0.0879(10)	0.194(3)	0.2790(6)	162(8)
O(4)–H(4B)···O(1) <sup>9</sup>	0.0877(10)	0.196(2)	0.2790(5)	156(5)

Symmetry codes: (1)  $-x + 1, -y + 1, -z$ , (2)  $x, y + 1, z - 1$ , (3)  $x, y + 1, z$ , (4)  $x - 1, y, z - 1$ , (5)  $x, y, z - 1$ , (6)  $x + 1, y, z$ , (7)  $x - 1, y - 1, z$ , (8)  $-x + 1, -y, -z + 1$ , (9)  $-x + 1, -y + 2, -z + 1$



**Fig. 3** Packing arrangement and the hydrogen bonds of  $[\text{Ni}(\text{TO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$



**Fig. 4** DSC, TG-DTG curves of the complex  $[\text{Ni}(\text{TO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot n$  with the heating rate  $10^\circ\text{C min}^{-1}$

### Thermogravimetric analysis

Typical DSC and TG-DTG curves for the complex with the heating rates of  $10^\circ\text{C min}^{-1}$  are shown in Fig. 4.

As the TG-DTG has shown, the first endothermic step is confirmed as the loss of four water molecules, and the lost amount is 15.15% (cal. 15.62%). The residues are further decomposed as nickel nitrate [11] at  $207^\circ\text{C}$  and the residue amount is 40.01% (cal. 39.64%). The final decomposition product is NiO and the residue amount is 16.73%, which is in good agreement with the calculated amount of 16.20%. The decomposition residues are identified by XPRD.

### Thermal analytical kinetics

In order to obtain the apparent activation energy ( $E_a$ ) and pre-exponential constant ( $A$ ) of the initial two decomposition stages of the complex, a multiple heating method is adopted. From the original data obtained, Kissinger method [24] and Ozawa's method [25] are utilized to calculate the  $E_a$  and  $A$ . The calculated results are listed in Table 4.

The value ( $T_{p0}$ ) of the peak temperature ( $T_p$ ) corresponding to  $\beta \rightarrow 0$  obtained by Eq. 1 taken from [21] is

351.90 K (the first step) and 429.65 K (the second step), respectively.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 \quad i = 1 - 4 \quad (1)$$

where  $b$  and  $c$  are coefficients.

The corresponding critical temperature of thermal explosion ( $T_b$ ) obtained from Eq. 2 taken from [26] is 359.84 and 437.36 K, respectively.

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{p0}}}{2R} \quad (2)$$

where  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $E_0$  is the value of  $E$  obtained by Ozawa's method.

The entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) are calculated according to Eqs. 3–6, and the values are listed in Table 5.

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (3)$$

$$\Delta H^\ddagger = E - RT \quad (4)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (5)$$

where  $k_B$  is the Boltzmann constant and  $h$  the Planck constant.

As shown in Table 5, the values of  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta H^\ddagger$  are all positive, indicating that the decomposition

**Table 5** The kinetic parameters of the initial two decomposition process

	The first step	The second step
$T_{p0}/^\circ\text{C}$	78.5	156.5
$E_k/\text{kJ mol}^{-1}$	132.09	209.6
$\lg(A_k)/\text{s}^{-1}$	17.21	23.23
$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	83.18	196.8
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	129.17	206.0
$\Delta G^\ddagger/\text{kJ mol}^{-1}$	99.92	121.4

**Table 4** The calculated results of apparent activation energy ( $E_a$ ) and pre-exponential constant ( $A$ )

	The first step		The second step	
	Kissinger	Flynn–Wall–Ozawa	Kissinger	Flynn–Wall–Ozawa
$E/\text{kJ mol}^{-1}$	132.09	131.37	209.6	206.3
$\lg(A)/\text{s}^{-1}$	17.21		23.23	0.9940
$r$	0.9981	0.9983	0.9935	
$Q (\times 10^3)$	3.716	0.7052	1.318	0.2483
$E_a$	109.2		208.0	

The heating rate ( $\beta$ ) is 5, 10, 15,  $20^\circ\text{C min}^{-1}$ , respectively. The maximum peak temperature ( $T_p$ ) of the first decomposition process in four TG-DTG curves are 86, 92, 95,  $97^\circ\text{C}$ , respectively. The maximum peak temperature ( $T_p$ ) of the second decomposition process in four TG-DTG curves are 162, 166, 170,  $172^\circ\text{C}$ , respectively.  $E_a$  apparent activation energy;  $A$  pre-exponential constant;  $r$  linear correlation coefficient;  $Q$  the standard mean square deviation

reaction for the title complex is not spontaneous and readily proceeds at high temperatures.

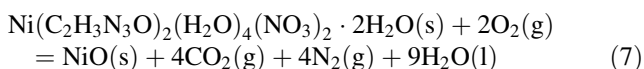
The standard enthalpy of formation

The constant-volume combustion energy ( $\Delta_c U$ ) of the complex was determined by six experiments and the method used was the same as that for calibration of the calorimeter with benzoic acid. The combustion energies of the complex were calculated by the formula

$$\Delta_c U = \frac{W\Delta T - aG - 5.983b}{m} \quad (6)$$

where  $\Delta_c U$  is the constant-volume combustion energy of the complex,  $W$  is the energy equivalent of the RBC-type II calorimeter (in  $\text{J K}^{-1}$ ),  $\Delta T$  the correct value of the temperature rising,  $a$  the length of actual Ni-Cr wire consumed (in cm),  $G$  the combustion enthalpy of Ni-Cr wire for ignition ( $0.9 \text{ J cm}^{-1}$ ),  $5.983$  the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of  $0.1000 \text{ mol L}^{-1}$  solution of NaOH (in  $\text{J mL}^{-1}$ ),  $b$  the volume in mL of consumed  $0.1000 \text{ mol L}^{-1}$  solution of NaOH and  $m$  the mass in grams of the sample. The calculated result is  $-6371.01 \pm 3.40 \text{ J g}^{-1}$ .

The standard enthalpy of combustion of the complex,  $\Delta_c H_m^\theta$  [ $[\text{Ni}(\text{TO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , s, 298.15 K), was referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.



The standard enthalpy of combustion of the complex was calculated by the following equations:

$$\Delta_c H_m^\theta = \Delta_c U + \Delta nRT \quad (8)$$

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \quad (9)$$

where  $n_g$  is the total amount in mole of gases present as products or as reactants,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T = 298.15 \text{ K}$ . The result is  $-2921.66 \pm 1.57 \text{ kJ mol}^{-1}$ .

The standard enthalpy of formation of the complex,  $\Delta_f H_m^\theta$  was calculated by Hess's law according to the above thermochemical equations (7):

$$\Delta_f H_m^\theta ([\text{Ni}(\text{H}_2\text{O})_4(\text{TO})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}) \\ = 4\Delta_f H_m^\theta (\text{CO}_2, \text{g}, 298.15 \text{ K}) + 9\Delta_f H_m^\theta (\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) \\ + 4\Delta_f H_m^\theta (\text{N}_2, \text{g}, 298.15 \text{ K}) + \Delta_f H_m^\theta (\text{NiO}, \text{s}, 298.15 \text{ K}) \\ - \Delta_c H_m^\theta ([\text{Ni}(\text{H}_2\text{O})_4(\text{TO})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}, \text{s}, 298.15 \text{ K})$$

when  $\Delta_f H_m^\theta (\text{CO}_2, \text{g}, 298.15 \text{ K}) = -393.51 \pm 0.13 \text{ kJ mol}^{-1}$  [24],  $\Delta_f H_m^\theta (\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) = -285.83 \pm 0.042 \text{ kJ mol}^{-1}$  [27], the result obtained is  $-1464.55 \pm 1.70 \text{ kJ mol}^{-1}$ .

## Conclusions

The single crystal structure of a new complex  $[\text{Ni}(\text{TO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 2(\text{H}_2\text{O})$  has been determined by X-ray diffractometer. Hydrogen bonds have significant effect to construct the three-dimensional net. The kinetic of the initial two decomposition stages has been investigated by TG-DTG. The thermal decomposition kinetic study is quite useful in the evaluation of thermal changes for the title complex at high temperatures. As an important data to evaluate the performance of the energetic material, the standard enthalpy of formation has been determined by a precise rotating-bomb calorimeter and the standard enthalpy of formation of the title complex is  $-1464.55 \pm 1.70 \text{ kJ mol}^{-1}$ .

## Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 294959. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: t44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

**Acknowledgements** We gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant Nos. 20771089 and 20813100), the National Natural Science Foundation of Shaanxi Province (Grant Nos. 2007B02 and SJ08B09), the Educational Committee of Shaanxi Province (No. 08JK459) and the Science and Technology Foundation of the National Defense Key Laboratory of Propellant and Explosive Combustion of China (Grant No. 51455010105QT3001).

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