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Thermal decomposition mechanism and thermodynamic properties of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$

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Abstract

The single crystal of nickel complex of 3-nitro-1,2,4-triazol-5-one (NTO), $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ was prepared and the crystal structure was determined by a four-circle X-ray diffractometer. Based on the results of thermal analysis, the thermal decomposition mechanism of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ was derived. From measurements of the enthalpy of solution in water of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ at 298.15 K, the standard enthalpy of formation, lattice enthalpy and lattice energy have been determined as $-(2585.6\pm4.5)$, -2832.59, and $-2797.58\,kJ\,mol^{-1}$, respectively.

Keywords: Crystal structure; Nickel complex; NTO; Thermal decomposition mechanism; Thermodynamic properties

1. Introduction

Much attention has been paid to 3-nitro-1,2,4-triazol-5-one (NTO) as a high energy and low sensitivity energetic material [1,2]. Its metal complexes also have some potential uses in ammunition [3–7]. Therefore, the authors prepared the single crystal of the nickel complex of NTO, determined its structure, studied its thermal decomposition mechanism and thermodynamic properties.

2. Experimental

2.1. Materials

$[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ used in this research work was prepared according to the following method: an appropriate amount of NTO was put into the distilled water (M:V = 1:4), then stirred and titrated with an aqueous solution of lithium hydroxide under 60 °C until the pH value of the mixture reached a value of 6. The resulting solution was gradually dropped into an aqueous solution of nickel sulfate at 60 °C to get green precipitates. The precipitates were recrystallized with distilled water at room temperature to obtain the green single crystal for X-ray measurement. Its purity was more than 99.6%. Dimensions of the single crystal were 0.15 mm × 0.15 mm × 0.20 mm.

2.2. Experimental equipment and conditions

The elemental analysis was performed on a MOD1106 (Carlo Erba, Italy) elemental analysis instrument. The infrared spectra of the decomposition residues were recorded in KBr discs on a 60 SXRFT-IR (Nicolet, USA) spectrometer.

In the determination of the structure of the single crystal, X-ray intensities were recorded by a CAD4PDP 11/44 automatic diffractometer with graphite, monochromatized Mo Kα radiation, $\lambda = 0.071073$ nm. Cell parameters were determined from 25 reflections. Data were collected by $\theta/2\theta$, scan mode in the range of $\theta = 2$–$25°$, $h = 0$–11, $k = 0$–16, $l = -7$ to 7, and the 1651 independent reflections were obtained, among which 1337 with $I > 3.0\sigma(I)$ were used for the determination and refinement of the crystal structure. Lorentz-polarization correction was applied but not for absorption correction. The coordinates of Ni atom were ob-

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tained by the Patterson method and those of non-hydrogen and hydrogen atoms were obtained by difference Fourier synthesis. Refinement was performed by the block-diagonal least-squares method using anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms.

The thermal decomposition process was studied using a TG technique on a Delta Series TGA7 (Perkin-Elmer, USA). The conditions of TG were as follows: sample mass ca. 1 mg; heating rate 10 °C min^{-1}; atmosphere, a flowing N_2/O_2 mixture with a ratio of 99%.

All measurements of the enthalpy of solution in deionized water were made using a Calvet microcalorimeter, type BT215 from SETARAM, France, and operated at 298.15 ± 0.005 K. The experimental precision and accuracy of enthalpies of solution were frequently checked by measuring the enthalpies of solution ($\Delta_{sol}H^{\circ}_{\infty}$) of crystalline KCl (NIST SRM1655) in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H^{\circ}_{\infty} = 17.217 \pm 0.053$ kJ mol^{-1} is in excellent agreement with that of $\Delta_{sol}H^{\circ}_{\infty} = 17.234$ kJ mol^{-1} reported in the literature [8].

3. Results and discussion

3.1. Crystal structure

The crystal structure was found to be monoclinic, which belongs to space group $P2_1/c$ with crystallographic parameters of $a = 0.9255(2)$ nm, $b = 1.4133(2)$ nm, $c = 0.6465(1)$ nm, $\beta = 88.42(2)^{\circ}$, $V = 0.8452$ nm^3, $Z = 2$, $D_c = 1.819$ g cm^{-3}, $\mu = 12.382$ cm^{-1}, $F(000) = 480$. The final $R = 0.030$, wR = 0.036 (unit weight), and $(\Delta/\sigma)_{max} = 0.01$.

The bond lengths and bond angles are summarized in Tables 1 and 2. The crystal structure and atom labeling are shown in Fig. 1.

The analytical results indicate that the formula of the molecule is $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$. It is central symmetrical, and Ni atom is at the symmetrical center. The Ni atom and six water molecules form an octahedron. Then combining it with two NTO anions, we can get $[Ni(H_2O)_6](NTO)_2$. There are two crystallization water molecules in the crystal.

The atoms in NTO anion are almost coplanar. The equation of the plane is

$$-0.047x + 0.0398y - 0.9981z + 3.6005 = 0$$

The bond distances of a five-membered ring of NTO anion tend to be equal. The bond lengths of N_1–C_1, N_3–C_1, N_3–C_2 and N_1–N_2 are almost equal, while the bond length of N_2–C_2 is a little shorter, which is the nearest double bond in the NTO anions, and that of N_4–C_2 is a little longer, which is the longest in the NTO anion. The calculated result indicates that the distance form Ni to the plane of NTO anion is 0.3299 nm. Thus the distance between two NTO anion planes is 0.6598 nm.

Table 1
Bond distances (nm)

Ni–O_{w1}	0.2080(5)
Ni–O_{w2}	0.2027(4)
Ni–O_{w3}	0.2018(5)
Ni–O'_{w1}	0.2080(5)
Ni–O'_{w2}	0.2027(4)
Ni–O'_{w3}	0.2018(5)
O–C_1	0.1270(4)
O_2–N_4	0.1209(10)
O_3–N_4	0.1220(4)
N_1–N_2	0.1366(4)
H_1–O_{w4}	0.2044(3)
H_1–N_1	0.0775(4)
H_{w11}–O_{w1}	0.0530(3)
H_{w11}–O_1	0.2580(2)
H_{w12}–O_{w1}	0.0919(15)
O_{w3}–O_{w4}	0.2771(9)
O_{w1}–O_{w4}	0.3070(2)
O_{w1}–O_1	0.2720(3)
O_{w1}–O_1	0.2980(5)
O_{w2}–O_2	0.2878(12)
O_{w2}–N_3	0.2734(14)
N_1–C_1	0.1360(5)
N_2–C_2	0.1298(11)
N_3–C_1	0.1350(5)
N_3–C_2	0.1337(8)
N_4–C_2	0.1450(3)
Hw_{12}–O_1	0.1842(15)
H_{w21}–O_{w2}	0.0833(13)
H_{w21}–N_3	0.1910(3)
H_{w22}–O_{w2}	0.0951(7)
H_{w22}–O_2	0.1959(8)
H_{w41}–N_2	0.1972(4)
H_{w42}–O_{w1}	0.2230(3)
H_{w31}–O_{w3}	0.0825(7)
H_{w31}–O_{w4}	0.1959(6)
O_{w3}–O_1	0.2690(2)
O_{w4}–N_1	0.2807(5)
O_{w4}–N_2	0.2871(5)
O_{w3}–H_{w32}	0.0893(5)
O_{w4}–H_{w41}	0.0926(3)
O_{w4}–H_{w42}	0.0975(8)
N_1–H_1	0.0775(4)
H_{w32}–O_{w3}	0.0893(5)
H_{w32}–O_1	0.1970(2)
H_{w42}–O_{w4}	0.09750(8)

3.2. Thermal decomposition mechanism of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$

The typical TG–DTG curve of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ is shown in Fig. 2. The DTG curve shows that the thermal decomposition process of the title compound can be divided into three stages. The first mass loss is 30.3% between 62.0 and 161.5 °C, which roughly coincides with the calculated value (31.3%) of losing eight water molecules from the complex. The IR spectrum of the residue at 170 °C shows the absorption peak at 3519 cm^{-1} was absent, which denotes that the complex has been dehydrated. This process can also be confirmed by the single crystal structure. The hydrogen bonds between water molecules and the Ni atom are easy

Table 2
Bond angles (°)

O_{w1}–Ni–O_{w2}	91.2(5)
O_{w1}–Ni–O_{w3}	89.3(7)
O_{w2}–Ni–O_{w3}	90.9(3)
N_2–N_1–C_1	111.0(2)
N_1–N_2–C_2	100.1(5)
C_1–N_3–C_2	102.0(1)
O_2–N_4–O_3	124.0(3)
O_{w4}–H_1–N_1	168.2(3)
O_{w1}–H_{w11}–O_1	135.0(5)
O_2–N_4–C_2	118.0(3)
O_3–N_4–C_2	118.2(7)
O_1–C_1–N_1	124.0(4)
O_1–C_1–N_3	128.0(4)
N_1–C_1–N_3	108.0(5)
N_2–C_2–N_3	119.1(6)
N_2–C_2–N_4	119.0(1)
O_{w1}–H_{w12}–O_1	159.0(2)
O_{w2}–H_{w21}–N_3	170.0(4)
O_{w2}–H_{w22}–O_2	162.1(8)
O_{w2}–H_{w22}–N_4	141.0(1)
N_3–C_2–N_4	122.0(1)
H_{w11}–O_{w1}–H_{w12}	110.0(3)
H_{w21}–O_{w2}–H_{w22}	93.2(5)
H_{w31}–O_{w3}–H_{w32}	106.5(6)
H_{w41}–O_{w4}–H_{w42}	106.4(8)
O_{w3}–H_{w31}–O_{w4}	167.9(4)
O_{w3}–H_{w32}–O_1	137.3(3)
O_{w4}–H_{w41}–N_2	162.9(3)
O_{w1}–H_{w42}–O_{w4}	144.1(8)

to be broken. The second process occurs between 161.5 and 342.0 °C, corresponding to the further decomposition of the dehydrated salt. The IR spectrum of the residue shows the absorption peak of –NO_2 has disappeared and the characteristic absorption peaks of $Ni(OCN)_2$ and $NiCO_3$ have formed after the decomposition peak appear at 2178, 1203, 1435 and 761 cm^{-1}, respectively. These observations indicate that the decomposition residue of this stage is a mixture. The amount

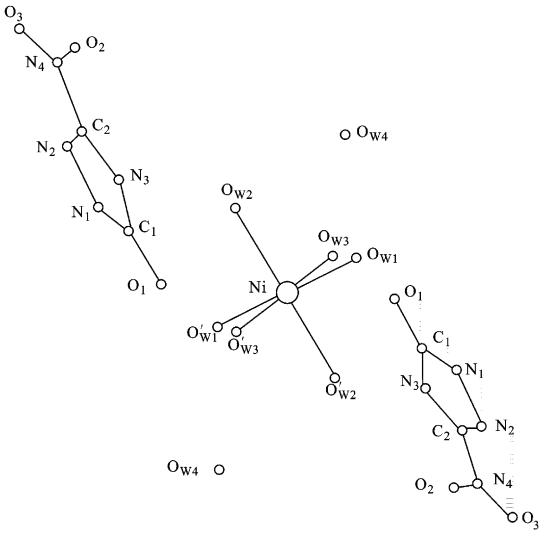

Fig. 1. Molecular structure of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$.

of each component cannot be determined from the present experiment and it is impossible to determine the decomposition change stoichiometrically. The third process is between 342.0 and 408.0 °C. The IR spectrum of the residue at 342.0 °C shows that a strong absorption peak at 443 cm^{-1} is assigned to NiO. At the end of this stage, the residue amount is in good agreement with the calculated amount of 16.2%.

On the basis of the experimental and calculated results, the thermal decomposition mechanisms of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ can be expressed as

$$[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O \xrightarrow{62.0\text{–}161.5^\circ C}$$

$$Ni(NTO)_2 \xrightarrow{161.5\text{–}342.0^\circ C} Ni(OCN)_2$$

$$+ NiCO_3 \xrightarrow{342.0\text{–}408.0^\circ C} NiO$$

3.3. Thermodynamic properties of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$

Results for the enthalpy of solution of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ in deionized water at 298.15 K are listed in Table 3.

Because $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ is completely ionized in aqueous solution, its ionization can be represented as

$$[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O \xrightarrow{\Delta_{sol}H^\circ_m} Ni^{2+}(aq, \infty) + 2NTO^-(aq, \infty) + 8H_2O(l) \quad (1)$$

In the above process, the greater values of r were used. Therefore, the mean of $\Delta_{sol}H^\circ_m$ in Table 3 can be considered at infinite dilution.

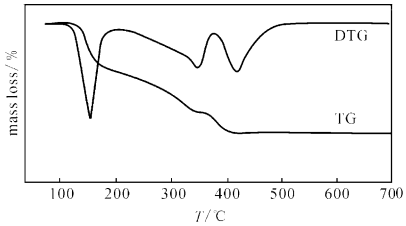

Fig. 2. TG–DTG curve of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$.

Table 3
Enthalpy of solution in water of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$ (cr) at 298.15 K

m (mg)	r	$\Delta_{sol}H^\circ_m$ (kJ mol^{-1})
3.870	59502	56.04
3.900	59044	56.30
4.100	56164	56.01
4.340	53058	56.24
4.860	47381	56.70
5.240	43945	56.35
5.700	40399	56.74
7.093	32465	56.71
Mean		56.39 ± 0.32

Note: $\Delta_{sol}H^\circ_m$ denotes the enthalpy of solution in water of $[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$, where m is the mass of $Ni(H_2O)_6](NTO)_2{\cdot}2H_2O$, and r the molar ratio $n(H_2O)/n\{[Ni(H_2O)_6](NTO)_2{\cdot}2H_2O\}$.

By substituting the mean of $\Delta_{sol}H^{\circ}_{m}$ listed in Table 3 and the reported values of $\Delta_f H^{\circ}_m(Ni^{2+}, aq, \infty) = -53.97\,kJ\,mol^{-1}$ [9]; $\Delta_f H^{\circ}_m(NTO^-, aq, \infty) = -(94.3 \pm 2.1)\,kJ\,mol^{-1}$ [10]; and $\Delta_f H^{\circ}_m(H_2O, l) = -285.83\,kJ\,mol^{-1}$ [9], into Eq. (2),

$$\Delta_{sol}H^{\circ}_{m} = \Delta_f H^{\circ}_m(Ni^{2+}, aq, \infty) + 2\Delta_f H^{\circ}_m(NTO^-, aq, \infty) + 8\Delta_f H^{\circ}_m(H_2O, aq, \infty) - \Delta_f H^{\circ}_m\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr, 298.15\,K\} \quad (2)$$

The following value is obtained:

$$\Delta_f H^{\circ}_m\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = -(2585.6 \pm 4.5)\,kJ\,mol^{-1}.$$

Setting $\Delta H^{\circ}_L\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}$ as the lattice enthalpy and $\Delta U^{\circ}_L\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}$ as the crystal lattice energy

$$Ni^{2+}(g) + 2NTO^-(g) + 8H_2O(g) \xrightarrow{\Delta H^{\circ}_L} [Ni(H_2O)_6](NTO)_2 \cdot 2H_2O(cr) \quad (3)$$

$$\Delta H^{\circ}_L\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = \Delta_f H^{\circ}_m\{[Ni(H_2O)_6] \cdot (NTO)_2 \cdot 2H_2O, cr, 298.15\,K\} - \Delta_f H^{\circ}_m(Ni^{2+}, g) - 2\Delta_f H^{\circ}_m(NTO^-, g) - 8\Delta_f H^{\circ}_m(H_2O, g) \quad (4)$$

$$\Delta U^{\circ}_L\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = \Delta H^{\circ}_L\{[Ni(H_2O)_6] \cdot (NTO)_2 \cdot 2H_2O, cr\} - \Delta n\,RT \quad (5)$$

where $\Delta_f H^{\circ}_m(Ni^{2+}, g) = 2930.14\,kJ\,mol^{-1}$ [9], $\Delta_f H^{\circ}_m(NTO^-, g) = -374.3\,kJ\,mol^{-1}$ [11], $\Delta_f H^{\circ}_m(H_2O, g) = -241.82\,kJ\,mol^{-1}$ [9], $\Delta n = -14$, $RT = 2.5\,kJ\,mol^{-1}$.

By substituting the above-mentioned data into Eqs. (4) and (5), the following values are obtained:

$$\Delta H^{\circ}_L\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = -2832.59\,kJ\,mol^{-1},$$
$$\Delta U^{\circ}_L\{[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = -2797.58\,kJ\,mol^{-1}$$

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