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Preparation, crystal structure, thermal decomposition mechanism and thermodynamic properties of $[Co(H_2O)_6](NTO)_2\cdot 2H_2O$

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Abstract

The single crystal of cobalt compound of 3-nitro-1,2,4-triazol-5-one (NTO) ($[Co(H_2O)_6](NTO)_2\cdot 2H_2O$) was prepared and the crystal structure has been determined by a four-circle X-ray diffractometer. The compound is monoclinic with space group Cc and unit cell parameters of $a = 2.3163\,(2)$ nm, $b = 0.6451\,(1)$ nm, $c = 1.4123\,(1)$ nm, $\beta = 123.96\,(1)^\circ$, $V = 1.7504\,(3)\ \mathrm{nm}^3$ and $Z = 4$. Based on the thermal analysis, the thermal decomposition mechanism of $[Co(H_2O)_6](NTO)_2\cdot 2H_2O$ has been derived. From measurements of the enthalpy of solution in water at 298.15 K, the standard enthalpy of formation, lattice enthalpy and lattice energy have been determined as $-(2594.7 \pm 4.5)$, -2753.19, and $-2718.19\ \mathrm{kJ\,mol^{-1}}$, respectively.

Keywords: 3-Nitro-1,2,4-triazol-5-one (NTO); Preparation; Crystal structure; Thermal decomposition mechanism; Thermodynamic properties

1. Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) is an explosive with high energy and low sensitivity to impact and friction. Los Alamos Laboratory began its research on the synthesis, physicochemical and explosive properties of NTO in 1980s [1,2]. The impact behavior and mechanism of initiation of NTO on impact has also been reported by Agrawal et al. [3] using drop-weight machine coupled with high-speed rotating mirror camera. Recently, much attention has been paid to the studies on the synthesis, properties and structure of its metal salts [4–8]. As a new high energy and low sensitivity energetic additive, NTO metal complexes can be used as one of the components of intermolecular explosives and propellants. When NTO salts were added to a formula system, their burning velocity and specific impulse are greatly improved, while the index of pressure decreases [9]. In this work, the authors prepared single crystal of cobalt salt of NTO, measured its structure, studied its thermal decomposition mechanism and its thermodynamic properties.

2. Experimental

2.1. Materials

NTO was prepared and purified by a reported method [10]. Its purity was more than 99.5%. Other chemicals were of analytical grade.

2.2. Preparation of $[Co(H_2O)_6](NTO)_2\cdot 2H_2O$

An appropriate amount of NTO was put into the distilled water ($M{:}V = 1{:}4$), which was then stirred and titrated with aqueous solution of lithium hydroxide at 60 °C until pH reached about 7. The prepared solution was gradually dropped to an aqueous solution of cobaltous nitrate at 60 °C to get brown–yellow precipitates. Single crystal suitable for X-ray measurement was obtained by recrystallization with distilled water at room temperature. Its purity was more than 99.6%. Anal. Calcd. for $[Co(H_2O)_6](NTO)_2\cdot 2H_2O$: Co 12.78, C 10.42, N 24.30, H 3.92; Found (%): Co 12.12, C 9.85, N 24.78, H 4.01. IR (KBr): $\nu_{C=O} = 1644\ \mathrm{cm^{-1}}$, $\nu^{as}_{NO_2} = 1509\ \mathrm{cm^{-1}}$, $\nu^{s}_{NO_2} = 1311\ \mathrm{cm^{-1}}$, $\nu_{M\text{–}O} = 327\ \mathrm{cm^{-1}}$, $\nu_{M\text{–}N} = 261\ \mathrm{cm^{-1}}$.

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Table 1
Crystal data and structure refinement for $[Co(H_2O)_6](NTO)_2 \cdot 2H_2O$

Empirical formula	$C_4H_{18}CoN_8O_{14}$
Formula weight ($g\,mol^{-1}$)	461.19
T (K)	297 (2)
Wavelength (nm)	0.071073
Crystal system	Monoclinic
Space group	Cc
a (nm)	2.3163 (2)
b (nm)	0.6451 (1)
c (nm)	1.4123 (1)
β (°)	123.96 (1)
V (nm^3), Z	1.7504 (3), 4
F (0 0 0)	948
D_c ($mg\,m^{-3}$)	1.750
μ (mm^{-1})	1.069
2θ range (°)	3.48–57.98
Index range	$0 \le h \le 31$, $0 \le k \le 8$, $-19 \le l \le 15$
Reflections collections	2589
Independent reflections	2528
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR_2 = 0.0605$
Largest diffraction peak and hole (e/nm^3)	310 and −181

2.3. Experimental equipment and conditions

Dimensions of the single crystal used for X-ray measurement were 0.60 mm × 0.46 mm × 0.32 mm. X-ray intensities were recorded by a Siemens P4 four-circle diffractometer with graphite-monochromatized Mo Kα radiation, $\lambda = 0.071073$ nm. Details of the crystal parameters, data collection and refinement are listed in Table 1.

The coordinates of Co atom were obtained by Patterson method and those of non-hydrogen and hydrogen atoms were got by difference Fourier synthesis. Refinement was performed by block-diagonal least-squares method using anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. All calculation was carried out with Siemens SHELXTL 5.10 program on a PII 350 computer.

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

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} and an atmosphere 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 (SETARAM, France) and operated at (298.15 ± 0.005) K. The experimental precision and accuracy of enthalpies of solution were frequently checked by a measurement of 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 [11].

3. Results and discussion

3.1. Crystal structure

Bond distances and angles for the complex are listed in Table 2. The crystal structure and atom labeling are shown in Fig. 1 and the packing of the molecules in the crystal lattice is illustrated in Fig. 2.

The analytical results indicate that $[Co(H_2O)_6](NTO)_2 \cdot 2H_2O$ is a central symmetrical molecule, and Co atom is at the center of the molecule. The Co atom and six water molecules form a six hydrated cobalt cation of octahedron. Then combining it with NTO anions, we can get the neutral molecule $[Co(H_2O)_6](NTO)_2$. There are two water molecules of crystallization in the crystal. Bond lengths of six coordination water molecules of Co^{2+} are between 0.2059 and 0.2115 nm, and the bond angles formed by two non-symmetrical oxygen atoms and Co^{2+} are nearly 90°. Therefore, the octahedron formed by the Co atom and the six oxygen atoms of water is slightly deformed.

Table 2
Bond distances (nm) and angles (°) for the complex

Co–O (10)	0.2059 (5)	Co–O (11)	0.2061 (6)
Co–O (9)	0.2063 (5)	Co–O (12)	0.2084 (6)
Co–O (7)	0.2107 (4)	Co–O (8)	0.2115 (4)
O (1)–C (1)	0.1267 (6)	O (2)–N (4)	0.1197(7)
O (3)–N (4)	0.1233 (7)	O (4)–C (3)	0.1263 (6)
O (5)–N (8)	0.1241 (7)	O (6)–N (8)	0.1205 (6)
N (1)–N (2)	0.1344 (7)	N (1)–C (1)	0.1387 (7)
N (2)–C (2)	0.1340 (7)	N (3)–C (2)	0.1309 (8)
N (3)–C (1)	0.1330 (7)	N (4)–C (2)	0.1468 (7)
N (5)–C (3)	0.1338 (7)	N (5)–N (6)	0.1391(6)
N (6)–C (4)	0.1259 (7)	N (7)–C (4)	0.1360 (7)
N (7)–C (3)	0.1385 (7)	N (8)–C (4)	0.1449 (7)
O(10)–Co–O (11)	87.9 (2)	O (10)–Co–O (9)	179.0 (4)
O (11)–Co–O (9)	91.1(3)	O (10)–Co–O (12)	92.7 (3)
O (11)–Co–O (12)	179.1 (2)	O (9)–Co–O (12)	88.3 (2)
O (10)–Co–O (7)	93.2 (2)	O (11)–Co–O (7)	91.8 (3)
O (9)–Co–O (7)	86.8 (2)	O (12)–Co–O (7)	88.8 (2)
O (10)–Co–O (8)	87.1(2)	O (11)–Co–O (8)	87.2 (2)
O (9)–Co–O (8)	92.9 (2)	O (12)–Co–O (8)	92.2 (3)
O (7)–Co–O (8)	179.0 (5)	N (2)–N (1)–C (1)	110.3 (5)
C (2)–N (2)–N (1)	100.3 (5)	C (2)–N (3)–C (1)	102.9 (4)
O (2)–N (4)–O (3)	126.1(5)	O (2)–N (4)–C (2)	115.7 (5)
O (3)–N (4)–C (2)	117.7 (5)	C (3)–N (5)–N (6)	111.7 (5)
C (4)–N (6)–N (5)	100.1 (5)	C (4)–N (7)–C (3)	100.4 (5)
O (6)–N (8)–O (5)	122.7 (5)	O (6)–N (8)–C (4)	118.6 (5)
O (5)–N (8)–C (4)	118.3 (5)	O (1)–C (1)–N (3)	129.7 (5)
O (1)–C (1)–N (1)	122.0 (5)	N (3)–C (1)–N (1)	108.4 (5)
N (3)–C (2)–N (2)	118.1 (5)	N (3)–C (2)–N (4)	124.0 (5)
N (2)–C (2)–N (4)	117.8 (5)	O (4)–C (3)–N (5)	125.7 (5)
O (4)–C (3)–N (7)	126.7 (6)	N (5)–C (3)–N (7)	107.6 (5)
N (6)–C (4)–N (7)	120.2 (5)	N (6)–C (4)–N (8)	119.9 (5)
N (7)–C (4)–N (8)	119.9 (5)		

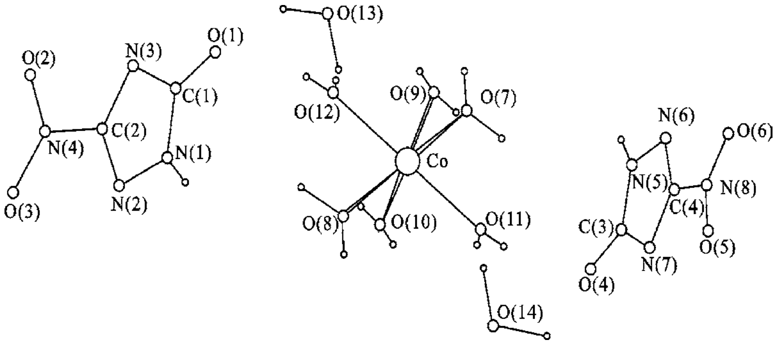

Fig. 1. Crystal structure of $[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$.

The atoms in NTO anion are all coplanar. The bond distances of the five-member ring of NTO anions tend to be equal. The bond lengths of N(3)–C(1), N(2)–C(2) and N(1)–N(2) are almost equal, but the bond length of N(3)–C(2) is a little shorter and that of N(4)–C(2) is a little longer, the latter is the longest one in the NTO anions. This result is almost the same as the structure data of NTO anion in ammonium [12], ethylenediammonium [13] and manganese salt [14], as well as the calculation of quantum chemistry [15].

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

The typical DSC and TG-DTG curves of $[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$ are shown in Figs. 3 and 4. The DTG curve shows that the thermal decomposition process of the title compound can be divided into two major stages. The first stage is a dehydration process, appearing as only one step. The total eight water molecules were lost. DSC curve indicates that this process is endothermic, and TG-DTG curves shows that the mass loss is 30.2% between 49.1 and 148.0 °C, which coincides with the calculated value (31.3%) of losing eight water molecules from the complex. The activation energy of dehydration obtained using Kissinger's method is 165.5 kJ mol^{-1}. The dehydrated coordination is unstable and further decomposition would happen when the compound being heated. Therefore, the second stage is the decomposition of anhydrous $Co(NTO)_2$ as well as the formation of Co_3O_4. The DSC curve shows that this stage is an exothermic process. First, the group of $-NO_2$ cleaved, then the NTO ring broke. The absorption bands at 2184 and 1195 cm^{-1} in IR spectrum of the decomposed residues at 325 °C confirm the presence of $Co(NCO)_2$. The further decomposed residue is $CoCO_3$, which finally changes into Co_3O_4. The activation energy for this stage is 127.5 kJ mol^{-1} obtained by Kissinger's method.

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

The mean of the enthalpy of solution $[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$ in deionized water at 298.15 K is (61.34 ± 0.32)

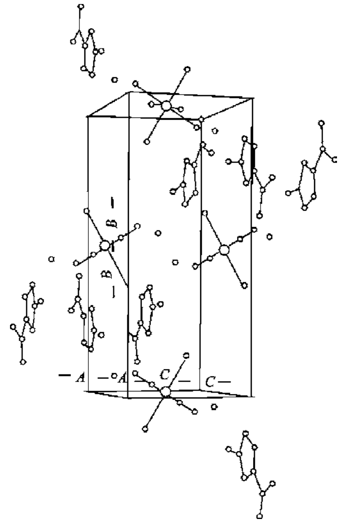

Fig. 2. Packing of molecular $[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$ in crystal lattice.

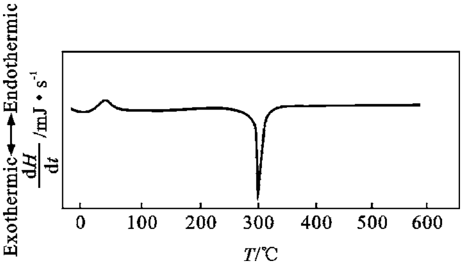

Fig. 3. DSC curve of $[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$.

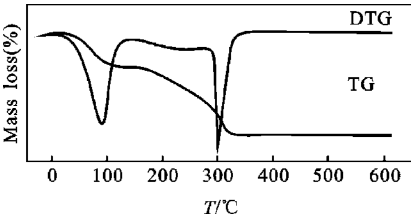

Fig. 4. TG-DTG curve of $[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$.

Table 3
Summary of the thermochemical data

Substance	State	$\Delta_f H_m^\circ$ (kJ mol^{-1}) (298.15 K)
Co^{2+}	aq.	−58.16 [16]
NTO^-	aq.	−(94.3 ± (2.1) [17]
H_2O	aq.	−285.83 [16]
$[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$	cr	−(2594.7 ± 4.5)[a]
Co^{2+}	g	2841.65 [16]
NTO^-	g	−374.3 [18]
H_2O	g	−241.82 [16]

[a] See text.

kJ mol^{-1}. The molar ratio $n(H_2O/n\{[Co(H_2O)_6](NTO)_2\cdot 2H_2O\}$ used in experiments are 18 190–47 651. Therefore, the mean of $\Delta_{sol}H_m^\circ$ can be considered at infinite dilution.

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

$$[Co(H_2O)_6](NTO)_2 \cdot 2H_2O \xrightarrow{\Delta_{sol}H_m^\circ} Co^{2+}(aq., \infty) + 2NTO^-(aq., \infty) + 8H_2O\,(1) \quad (1)$$

By substituting the mean of $\Delta_{sol}H_m^\circ$ and the reported values listed in Table 3 into the following equation:

$$\begin{aligned}\Delta_f H_m^\circ\{&[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr, 298.15\,K\}\\ &= \Delta_f H_m^\circ(Co^{2+}, aq., \infty) + 2\Delta_f H_m^\circ(NTO^-, aq., \infty)\\ &\quad + 8\Delta_f H_m^\circ(H_2O, aq., \infty) - \Delta_{sol}H_m^\circ \qquad (2)\end{aligned}$$

the following value is obtained:

$$\begin{aligned}\Delta_f H_m^\circ\{&[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}\\ &= -(2594.7 \pm 4.5)\,kJ\,mol^{-1}\end{aligned}$$

Setting $\Delta H_L^\circ\{[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}$ as the lattice enthalpy in forming the crystal $[Co(H_2O)_6](NTO)_2{\cdot}2H_2O$ from Co^{2+} (g), NTO^- (g) and H_2O (g) at 298.15 K and $\Delta U_L^\circ\{[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}$ as the crystal lattice energy:

$$Co^{2+}(g) + 2NTO^-(g) + 8H_2O(g) \xrightarrow{\Delta H_L^\circ} [Co(H_2O)_6](NTO)_2 \cdot 2H_2O(cr) \qquad (3)$$

we have

$$\begin{aligned}\Delta H_L^\circ\{&[Co(H_2O)_6](NTO)_2 \cdot H_2O, cr\}\\ &= \Delta_f H_m^\circ\{[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr, 298.15\,K\}\\ &\quad - \Delta_f H_m^\circ(Co^{2+}, g) - 2\Delta_f H_m^\circ(NTO^-, g)\\ &\quad - 8\Delta_f H_m^\circ(H_2O, g) \qquad (4)\end{aligned}$$

and

$$\begin{aligned}\Delta U_L^\circ\{&[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}\\ &= \Delta H_L^\circ\{[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} - \Delta nRT \qquad (5)\end{aligned}$$

where $\Delta n = -11$, $RT = 2.5\,kJ\,mol^{-1}$.

By substituting the data in Table 3 and the values of Δn and RT into Eqs. (4) and (5), the following values are obtained:

$$\begin{aligned}\Delta H_L^\circ\{&[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}\\ &= -2753.19\,kJ\,mol^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_L^\circ\{&[Co(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\}\\ &= -2718.19\,kJ\,mol^{-1}\end{aligned}$$

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