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Thermochimica Acta 352–353 (2000) 111–115

thermochimica acta

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Preparation, crystal structure and thermal decomposition process of $[Y(NTO)_2\ NO_3(H_2O)_5]\cdot 2H_2O$

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Received 2 June 1999; received in revised form 20 August 1999; accepted 24 September 1999

Abstract

$[Y(NTO)_2\ NO_3(H_2O)_5]\cdot 2H_2O$ was prepared by mixing the aqueous solution of lithium 3-nitro-1,2,4-triazol-5-onate and the dilute nitric acid solution of yttrium oxide. The single crystal structure has been determined by a four-circle X-ray diffractometer. The crystal is monoclinic, space group Cm with crystal parameters of a=0.6773(2) nm, b=2.0866(2) nm, c=0.6551(1) nm, β=102.98(2)°, V=0.9021(1) nm, Z=2, D_c=1.970 g cm^{-3}, μ=33.487 cm^{-1}, $F(000)$=540. The final R is 0.032. Based on the thermal analysis, the thermal decomposition process of $[Y(NTO)_2\ NO_3(H_2O)_5]\cdot 2H_2O$ has been derived.

Keywords: Crystal structure; Preparation; Thermal decomposition process; Yttrium complex of NTO

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 salts also have some potential uses in ammunition [3–7]. Therefore, the authors have prepared the single crystal of Yttrium salt of NTO, measured its structure and studied its thermal decomposition process.

2. Experimental

2.1. Materials

$[Y(NTO)_2\ NO_3(H_2O)_5]\cdot 2H_2O$ used in this research work was prepared according to the following method: an appropriate amount of NTO was put into the distilled water, then stirred and titrated with an aqueous solution of lithium hydroxide at 60°C until pH reached ca. 7. The prepared solution was gradually dropped into a dilute nitric acid solution of yttrium oxide at 60°C to yield the precipitate. The precipitate was recrystallized with distilled water at room temperature to obtain a yellow single crystal for X-ray measurement. Its purity was better than 99.6%. Dimensions of the single crystal were $0.1\times0.15\times0.20$ mm^3.

2.2. Experimental equipment and conditions

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$K\alpha$ radiation, λ=0.071073 nm. Cell

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PII: S0040-6031(99)00447-5

parameters were determined from 25 reflections. Data were collected by $\omega/2\theta$, scan mode in the range of 2°h {⩽}θ{⩽}25°, h=0–8, k=0–24, l=−7–7, and 856 independent reflections were got, among which 848 with I>3.0σ (I)are used for the determination and refinement of crystal structure. The coordinates of Y atom were obtained by the Patterson method and those of non-hydrogen and hydrogen atoms were obtained by difference Fourier synthesis. Refinement was performed by block-diagonal least-square methods 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 flowing N_2/O_2 mixture (with a ratio in air). The infrared spectra of the decomposition residues were recorded in KBr discs on a 60 SXR FT–IR spectrometer (Nicolet, USA) at 4 cm^{-1} resolution.

3. Results and discussion

3.1. Crystal structure

The crystal structure was found to be monoclinic, which belongs to space group Cm with crystallographic parameters of a=0.6773(2) nm, b=2.0866(2) nm, c=0.6551(1) nm, β=102.98(2)°, V=0.9021(1) nm, Z=2, D_c=1.970 g cm^{-3}, μ=33.487 cm^{-1}, F(000)=540. The final R=0.032, R_w=0.037(unit weight), and $(\Delta/\sigma)_{max}$=0.12.

Table 1
Positional parameters and B_{eq} (nm^2)

Atoms	x	y	z	B_{eq}
Y	0.992	0.0000	0.985	0.0154(1)
O01	1.468(1)	0.0510(2)	1.467(1)	0.041(1)
Ow1	0.7247(9)	0.0704(3)	0.8751(9)	0.038(1)
O02	1.351(1)	0.0000	1.180(1)	0.027(2)
Ow2	0.916(1)	0.0000	0.610(1)	0.027(2)
Ow3	1.1637(8)	−0.0868(3)	0.8766(8)	0.028(1)
Ow4	0.5124(8)	0.1357(3)	0.1246(9)	0.029(1)
O11	0.9929(9)	−0.0663(2)	1.2624(8)	0.027(1)
O12	1.037(2)	−0.3173(3)	1.579(1)	0.057(2)
O13	1.068(2)	−0.2422(3)	1.8103(9)	0.079(3)
N	1.430(1)	0.0000	1.377(2)	0.028(2)
N11	1.007(1)	−0.1750(3)	1.1745(9)	0.027(1)
N12	1.015(1)	−0.2331(3)	1.2706(9)	0.023(1)
N13	1.025(1)	−0.1509(2)	1.506(1)	0.021(1)
N14	1.043(1)	−0.2605(3)	1.630(1)	0.037(2)
C11	1.007(1)	−0.1261(3)	1.310(1)	0.019(2)
C12	1.025(1)	−0.2132(3)	1.474(2)	0.030(2)
Hw11	0.7070	0.0996	1.0000	0.04
H11	1.0410	−0.1679	1.0000	0.04
Hw31	1.1250	−0.1171	0.7910	0.04
Hw32	1.2910	−0.0820	0.8750	0.04
Hw41	0.5410	0.1328	0.2910	0.04
Hw42	0.4160	0.0996	0.0820	0.04
Hw12	0.5820	0.0332	0.8750	0.04
Hw2	0.9359	−0.0378	0.5410	0.04

The atom coordinates, thermal parameters, bond lengths and bond angles are summarized in Tables 1–3. The crystal structure and atom labeling are shown in Fig. 1 and the packing of the molecule in crystal lattice is illustrated in Fig. 2.

The analytical results indicate that two carbonyls of NTO anion, one NO_3^- and five water molecules are coordinated to Y^{3+}. The coordinate bond lengths are between 0.2283 and 0.2478 nm, so the distorted dode-

Table 2
Bond distances (nm)

Y–Ow1	0.2315(7)	N11–N12	0.1362(8)	Ow3–Hw32	0.0871(6)
Y–Ow1′	0.2315(7)	N11–C11	0.1350(9)	Ow4–Hw41	0.1066(6)
Y–O02	0.2478(7)	N12–C12	0.139(1)	Ow4–Hw42	0.0994(5)
Y–Ow2	0.2398(7)	N13–C11	0.137(1)	N–O01	0.1217(7)
Y–Ow3	0.2349(6)	N13–C12	0.1318(8)	N–O01′	0.1217(7)
Y–Ow3′	0.2349(6)	N14–C12	0.141(2)	N–O02	0.129(1)
Y–O11	0.2283(6)	Ow1–Hw11	0.1048(6)		
Y–O11′	0.2283(6)	Ow1–Hw12	0.1239(6)		
O11–C11	0.1282(8)	Ow2–Hw2	0.0934(4)		
O12–N14	0.123(1)	Ow2–Hw2′	0.0934(4)		
O13–N14	0.1218(9)	Ow3–Hw31	0.0847(6)		

Table 3
Bond angles (°)

Ow1–Y–Ow1′	78.7(2)	O02–Y–O11	76.3(2)	O11–C11–N11	125.9(6)
Ow1–Y–O02	140.2(2)	O02–Y–O11′	76.3(2)	O11–C11–N13	125.6(7)
Ow1–Y–Ow2	73.2(3)	Ow2–Y–Ow3	72.3(2)	N11–C11–N13	108.6(6)
Ow1–Y–Ow3′	143.2(2)	Ow2–Y–Ow3′	72.3(2)	N12–C12–N13	116.8(7)
Ow1–Y–Ow3	79.8(3)	Ow2–Y–O11	141.1(1)	N12–C12–N14	117.9(6)
Ow1–Y–O11′	119.7(2)	Ow2–Y–O11′	141.1(1)	N13–C12–N14	125.3(8)
Ow1–Y–O11	74.1(2)	Ow3–Y–Ow3′	101.0(2)	Hw11–Ow1–Hw12	98.0(5)
Ow1–Y–O02	140.2(2)	Ow3–Y–O11	81.9(2)	Hw2–Ow2–Hw2′	115.8(8)
Ow1–Y–Ow2	73.2(3)	Ow3–Y–O11′	142.7(2)	Hw31–Ow3–Hw32	103.8(6)
Ow1–Y–Ow3	79.8(3)	O11–Y–O11′	74.7(2)	Hw41–Ow4–Hw42	101.7(6)
Ow1–Y–Ow3′	143.2(2)	N12–N11–C11	112.1(6)	O01–N–O01′	122.3(9)
Ow1–Y–O11	74.1(2)	N11–N12–C12	99.6(5)	O01–N–O02	118.8(5)
Ow1–Y–O11′	119.7(2)	C11–N13–C12	103.0(7)	O01′–N–O02	118.8(5)
O02–Y–Ow2	119.2(3)	O12–N14–O13	123.6(8)		
O02–Y–Ow3	70.1(2)	O12–N14–C12	119.2(7)		
O02–Y–Ow3′	70.1(2)	O13–N14–C12	117.2(7)		

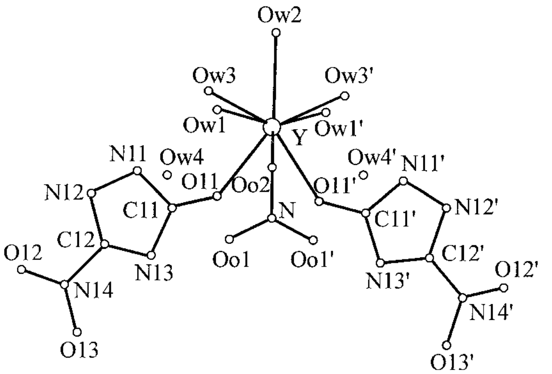
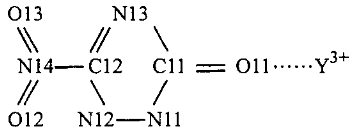
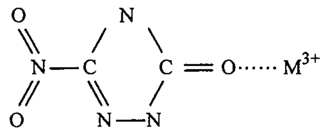


Fig. 1. Crystal structure of $[Y(NTO)_2\ NO_3(H_2O)_5]\cdot 2H_2O$.

cahedron is formed. The coordinate bond length from Y^{3+} to O02 in the NO_3^- is the longest one (0.2478 nm), and the shortest bond length is from Y^{3+} to O11 in the NTO^- (0.1283 nm). It is even much shorter than the coordinate bond length of carbonyl oxygen atom and metal in the reported complex of NTO and metal, they are between 0.2305 and 0.2680 nm [4,8,9]. The structure analysis shows that the bond length of C12–N13 (0.1318 nm) is shorter than C11–N13 (0.137 nm), C12–N14 (0.141 nm), C12–N12 (0.139 nm), N11–N12 (0.1362 nm) and C11–N11 (0.135 nm), so we can have the following structure of NTO ring:



and it's conjugative effect is better than the reported NTO ring [4,8,10,11]



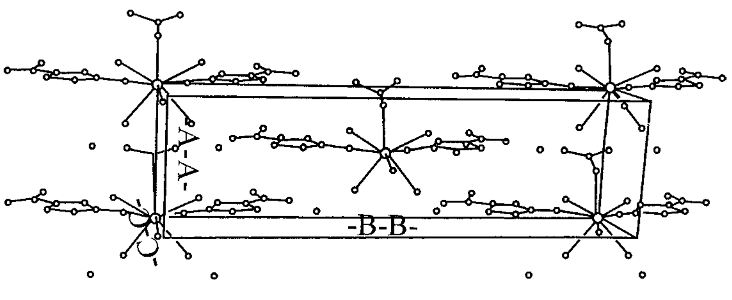


Fig. 2. Packing of the molecule $[Y(NTO)_2\ NO_3(H_2O)_5]\cdot 2H_2O$ in the crystal lattice.

Since the free moving of electrons in the NTO ring are easier, and the NTO ring gets the induction effect of Y^{3+}, the electron atmosphere density between O11... Y^{3+} is thicker and this coordinate bond length must be shorter than those in reported NTO–metal complexes [4,8,10,11]. The same is true of the fact of experiment.

According to the calculation, the atoms in NTO anion are all coplanar, and Ow2, Y, O02, N are on the symmetry surface of crystal. The equations of the planes are as follows:

$$0.9815x - 0.0159y - 0.1906z - 5.8395 = 0 \text{ (the plane of } NO_3^-\text{) (I)}$$

$$0.9859x - 0.0266y - 0.1652z + 6.1496 = 0 \text{ (the plane of NTO ring) (II)}$$

The symmetry plane of crystal (III)

The dihedral angle between plane I and plane III is 90°; because the plane III is the symmetry surface of two NTO ring, the planes of two NTO ring are coplanar, and the dihedral angle between plane II and plane III is also 90°, while between plane I and plane II is 159.36°.

The analytical results also indicate that there are two water of crystalization in the crystal, Ow4 and Ow4′ in two water of crystallization linked $[Y(NTO)_2NO_3(H_2O)_5]$ through hydrogen bond as below:

$$\underbrace{\mathrm{Ow1}\xrightarrow{0.1048\,\mathrm{nm}}\mathrm{Hw11}\overset{0.1858\,\mathrm{nm}}{\cdots\cdots\cdots}\mathrm{Ow4}}_{0.277\,\mathrm{nm}},\ \angle \mathrm{Ow1Hw11Ow4} = 142.6^\circ$$

$$\underbrace{\mathrm{O02}\overset{0.2248\,\mathrm{nm}}{\cdots\cdots\cdots}\mathrm{Hw42}\xrightarrow{0.0994\,\mathrm{nm}}\mathrm{Ow4}}_{0.309\,\mathrm{nm}},\ \angle \mathrm{O02Hw42Ow4} = 141.2^\circ$$

The title complex $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$ is formed.

3.2. Process of thermal decomposition of $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$

The TG–DTG curves for $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$ are shown in Fig. 3. The DTG curve shows that there are five processes at temperatures higher than 72. The first endothermic process is at 72–97°C. The TG curve shows that the mass loss corresponding to this temperature range is 6.0% which roughly coincides with the value of 6.7%, calculated for the loss of two water molecules from the complex. The second endothermic process is at 97–168°C, the mass loss is 16.2%, which coincides with the calculated value of 16.8%, corresponding to the loss of five water molecules.

Further decomposition of the dehydrated complex occurs at 168–222°C, the characteristic absorption peak of NO_3^- at 1384 cm^{-1} has disappeared and the characteristic absorption peaks of $Y_2(CO_3)_3$ and polymers containing the –CO–NH-group has formed after the decomposition peak appear at 1518 and 839, 3410, 1651, 1558 and 1384 cm^{-1}, respectively. The next decomposition is at 222–338°C, the characteristic absorption peak of $Y_2(CO_3)_3$ also appeared after this process. The characteristic absorption peak of the residue formed after the last process (338–492°C) at 561 and 401 cm^{-1} is assigned to Y_2O_3. At the end of this stage, the residue amounted to 22%. This value is in good agreement with the calculated amount of 21.1%.

On the basis of experimental and calculated results, the thermal decomposition of $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$ is postulated to proceed as follows:

$$\begin{aligned}&[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O\\&\xrightarrow[72-97^\circ C]{}[Y(NTO)_2NO_3(H_2O)_5]\\&\xrightarrow[97-168^\circ C]{}Y(NTO)_2NO_3\\&\xrightarrow[168-222^\circ C]{}Y_2(CO_3)_3\text{ (a little) }+\text{polymers}\\&\xrightarrow[222-338^\circ C]{}Y_2(CO_3)_3\xrightarrow[338-492^\circ C]{}Y_2O_3\end{aligned}$$

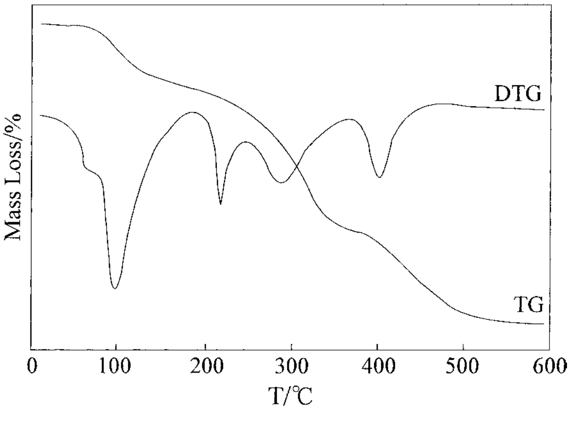


Fig. 3. TG–DTG curve of $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$.

4. Conclusion

The single crystal structure of $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$ was studied. We have found that the conjugative effect of NTO ring in $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$ is better than the reported NTO ring in the other complexes. Because the free moving of electrons in the NTO ring are easier, and the NTO ring gets the induction effect of Y^{+3}, the electron atmosphere density between $O\ldots Y^{+3}$ is thicker and this coordinate bond length must be shorter than those in the reported NTO–metal complexes. The fact of thermal decomposition show that the final decomposition temperature of $[Y(NTO)_2NO_3(H_2O)_5]\cdot 2H_2O$ is higher.

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