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Preparation, crystal structure, thermal decomposition mechanism and thermodynamical properties of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ and $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$

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Abstract

$[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ was prepared by mixing the aqueous solution of lithium 3-nitro-1, 2, 4-triazol-5-onate and the dilute nitric acid solution of ytterbium oxide. The single crystal structure was determined by a four-circle X-ray diffractometer. The crystal is monoclinic, space group C2/*c* with crystal parameters of $a = 3.6931$ (5)nm, $b = 0.6683(10)$ nm, $c = 2.5656(3)$ nm, $\beta = 130.974(5)^\circ$, $V = 4.7811(11)$ nm^3, $Z = 8$, $\mu = 40.17$ cm^{-1}, $F(000) = 2850$, $D_c = 2.013$ g cm^{-2}, and $\lambda(\mathrm{Mo}K_\alpha) = 0.071073$ nm. The final R is 0.0258. $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ was prepared by mixing the aqueous solution of 3-nitro-1, 2, 4-triazol-5-one and the excessive strontium carbonate. The single crystal structure was determined by a four-circle X-ray diffractometer. The crystal is monoclinic, space group $P2_1/c$ with crystal parameters of $a = 1.1034(1)$ nm; $b = 2.2742(2)$ nm, $c = 0.63398(9)$ nm, $\beta = 101.798(13)^\circ$, $V = 1.5573(4)$ nm^3, $Z = 4$, $D_c = 1.936$ g cm^{-3}, $\mu = 35.45$ cm^{-1}, $F(000) = 912$, $\lambda(\mathrm{Mo}K_\alpha) = 0.071073$ nm. The final R is 0.0347. Based on the results of thermal analysis, the thermal decomposition mechanism of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ and $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ were derived. From measurements of the enthalpy of solution of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ and $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ in water at 298.15 K, the standard enthalpy of formation, lattice energy, lattice enthalpy and standard enthalpy of dehydration have been determined as $-(3853.3 \pm 6.8)$ and $-(2545.2 \pm 4.7)$, -4596 and -2114, -4631 and -2136, 391 and 67.2 kJ mol^{-1}, respectively. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Enthalpy of solution; NTO salt; Standard enthalpy of formation; Thermal decomposition mechanism

1. Introduction

Much attention has been paid to 3-nitro-1, 2, 4-triazol-5-one (NTO) and its metal salts as a high energy and low sensitivity energetic material [1–3]. Therefore the authors prepared the single crystal of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ and $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$, determined their structure and studied their thermal decomposition mechanism and thermodynamic properties.

2. Experimental

2.1. Materials

$[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ 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 under 60°C until pH reached a value of 6–7. The resulting solution was gradually dropped into a dilute nitric acid solution of ytterbium oxide at 60°C, then stirred and heated at

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60°C for 30 min. This solution was allowed to stand for 10 h until yellow precipitate formed. The precipitate was recrystallized with distilled water at room temperature to obtain the yellow single crystal for X-ray measurement. Its purity was >99.6%. Dimensions of the single crystal were $0.46 \times 0.37 \times 0.32\ \mathrm{mm}^3$. The conductivity of deionized water used in the experiment was $5.48 \times 10^{-8}\ \mathrm{Scm}^{-1}$.

$[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ 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 strontium carbonate added in excess at 60°C. When carbon dioxide evolution ceased, the resulting solution was stirred and heated at 60°C for 30 min, then filtered off while still hot. The precipitate was then dissolved in ethyl alcohol, and the undissolved $SrCO_3$ was separated. This solution was allowed to stand for 8 h, until a yellow precipitate formed. The precipitate was recrystallized from distilled water in a Petri dish at 25°C to obtain the yellow single crystal for X-ray measurement. Its purity was >99.6%. Dimensions of the single crystal were $0.56 \times 0.32 \times 0.14\ \mathrm{mm}^3$. The conductivity of deionized water used in the experiment was $5.48 \times 10^{-8}\ \mathrm{Scm}^{-1}$.

2.2. Experimental equipment and conditions

In the determination of the structure of the single crystal, X-ray intensities were recorded by a Siemens P_4 automatic diffractometer with graphite, monochromatized MoK_α radiation, $\lambda = 0.071073$ nm. The 5756 independent reflections were obtained in the range of $3 \leq 2\theta \leq 56°$, out of which 4570 with $I > 2\sigma(I)$ were used for the determination and refinement of the crystal structure of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$. The 3202 independent reflections were obtained in the range of $4.18 \leq 2\theta \leq 52.98°$, out of which 1915 with $I > 2\sigma(I)$ were used for the determination and refinement of crystal structure of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$. The coordinates of Yb and Sr atoms were obtained by a direct method and those of the other atoms 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 of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ was studied on a TGA-DTA apparatus (TA, USA), and the thermal decomposition process of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ was studied on a Delta Series TGA 7 (Perkin–Elmer, USA). The conditions of TG and DTA were as follows: sample mass ca. 1 mg; heating rate 10°C min^{-1}; atmosphere, a flowing N_2/O_2 mixture (with the same ratio as in air). The DSC experiments were carried out with a model CDR-1 differential scanning calorimeter with an aluminium cell (diameter 5 mm, length 3 mm), whose side was rolled up. The conditions of DSC measurement were as follows: sample mass ca. 1 mg; heating rate 10°C min^{-1}; atmosphere static air; reference sample, α-Al_2O_3; thermocouple plate, Ni/Cr–Ni/Si. 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.

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 ($\Delta_{sol}H^0_\infty$) of crystalline KC1 in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H^0_\infty = (17.217 \pm 0.053)\ \mathrm{kJ\ mol}^{-1}$ is in excellent agreement with that of $\Delta_{sol}H^0_\infty = 17.234\ \mathrm{kJ\ mol}^{-1}$, reported in the literature [4].

3. Results and discussion

3.1. Crystal structure of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$

The crystal structure of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ was found to be monoclinic, which belongs to space group $C2/c$ with crystallographic parameters of $a = 3.6931(5)$ nm, $b = 0.6683(10)$ nm, $c = 2.5656(3)$ nm, $\beta = 130.974(5)°$, $V = 4.7811(11)\ \mathrm{nm}^3$, $Z = 8$, $\mu = 40.17\ \mathrm{cm}^{-1}$, $F(000) = 2850$, and $D_c = 2.013\ \mathrm{g\ cm}^{-3}$. The final $R = 0.0258$, WR = 0.0815.

The atomic coordinates, thermal parameters, bond lengths and bond angles are summarized in Tables 1–3. The molecular structure and atom labelling are shown in Fig. 1, the packing of the molecule in the crystal lattice and the coordination polyhedron of Yb^{3+} are illustrated in Figs. 2 and 3.

The results indicate that four water molecules and the three carbonyls of three NTO anions are coordi-

Table 1
Atomic coordinates and thermal parameters ($\times 10^3$, in nm^2)

Atoms	x	y	z	U_{eq}
Yb	0.1637(1)	0.4254(1)	0.2043(1)	0.20(1)
O(1)	0.0854(1)	0.3630(7)	0.1316(2)	0.40(1)
O(2)	0.0125(2)	0.1743(12)	−0.1122(3)	0.79(2)
O(3)	−0.0579(2)	0.1222(9)	−0.1456(2)	0.57(1)
O(4)	0.1861(1)	0.3141(6)	0.1482(2)	0.30(1)
O(5)	0.2333(2)	0.4386(8)	0.0047(2)	0.47(1)
O(6)	0.1643(2)	0.3422(9)	−0.0895(2)	0.58(1)
O(7)	0.2334(1)	0.3211(7)	0.3035(2)	0.35(1)
O(8)	0.4093(1)	0.3375(9)	0.5137(2)	0.53(1)
O(9)	0.3973(2)	0.3560(9)	0.5855(2)	0.54(1)
O(10)	0.1297(1)	0.6830(7)	0.1245(2)	0.36(1)
O(11)	0.2179(1)	0.6924(7)	0.2462(2)	0.43(1)
O(12)	0.1493(2)	0.5612(7)	0.2687(2)	0.39(1)
O(13)	0.1540(2)	0.0959(7)	0.2172(2)	0.53(1)
O(14)	−0.0037(2)	0.3259(13)	0.1529(3)	0.93(2)
O(15)	0.4480(2)	0.8897(12)	0.6700(3)	0.79(2)
O(16)	0.4127(2)	1.1053(9)	0.7208(2)	0.55(1)
O(17)	0.1761(2)	0.1896(8)	0.3879(2)	0.41(1)
O(18)	0.1953(1)	0.8982(7)	0.3340(2)	0.34(1)
O(19)	0.5000	0.5333(34)	0.7500	1.33(23)
N(1)	0.0045(1)	0.2896(7)	0.0467(2)	0.31(1)
N(2)	−0.0269(1)	0.2348(7)	−0.0218(2)	0.29(1)
N(3)	0.0490(2)	0.2680(7)	0.0180(2)	0.31(1)
N(4)	−0.0158(2)	0.1711(8)	−0.1024(3)	0.41(1)
N(5)	0.1298(2)	0.3183(8)	0.0282(2)	0.29(1)
N(6)	0.1295(2)	0.3349(8)	−0.0251(2)	0.31(1)
N(7)	0.2055(2)	0.3495(7)	0.0780(2)	0.25(1)
N(8)	0.1923(2)	0.3802(8)	−0.0282(2)	0.33(1)
N(9)	0.2598(2)	0.3493(7)	0.4147(2)	0.29(1)
N(10)	0.3022(2)	0.3563(8)	0.4803(2)	0.30(1)
N(11)	0.3141(1)	0.3338(7)	0.4040(2)	0.22(1)
N(12)	0.3822(2)	0.3463(8)	0.5273(2)	0.33(1)
C(1)	0.0502(2)	0.3095(8)	0.0703(3)	0.30(1)
C(2)	0.0025(2)	0.2252(9)	−0.0335(3)	0.30(1)
C(3)	0.1748(2)	0.3273(8)	0.0895(2)	0.24(1)
C(4)	0.1758(2)	0.3531(8)	0.0097(3)	0.25(1)
C(5)	0.2667(2)	0.3336(8)	0.3687(2)	0.24(1)
C(6)	0.3319(2)	0.3462(8)	0.4690(2)	0.24(1)

nated with Yb^{3+}. The coordinated bond lengths are between 0.2207 and 0.2351 nm and the pentagonal bipyramid is formed. The bond length from Yb to O11 (the water molecule) is the longest one (0.2351 nm), and the shortest bond length is the Yb–O4 distance in the NTO (0.2207 nm). The others are Yb–O7 (0.2235 nm), Yb–O13 (0.2289 nm), Yb–O1 (0.2223 nm), Yb–O12 (0.2235 nm) and Yb–O10 (0.2315 nm). All of these are typical coordinated bond lengths.

Table 2
Bond distances (in nm)

Yb–O(4)	0.2207(3)	Yb–O(1)	0.2223(4)
Yb–O(7)	0.2235(4)	Yb–O(12)	0.2235(4)
Yb–O(13)	0.2289(5)	Yb–O(10)	0.2315(4)
Yb–O(11)	0.2351(4)	O(1)–C(1)	0.1269(6)
O(2)–N(4)	0.1225(7)	O(3)–N(4)	0.1222(6)
O(4)–C(3)	0.1274(6)	O(5)–N(8)	0.1218(6)
O(6)–N(8)	0.1215(6)	O(7)–C(5)	0.1273(6)
O(8)–N(12)	0.1218(6)	O(9)–N(12)	0.1221(6)
N(1)–C(1)	0.1374(6)	N(1)–N(2)	0.1377(6)
N(2)–C(2)	0.1305(7)	N(3)–C(2)	0.1342(6)
N(3)–c(1)	0.1342(7)	N(4)–C(2)	0.1464(7)
N(5)–C(3)	0.1345(6)	N(5)–N(6)	0.1363(6)
N(6)–C(4)	0.1317(6)	N(7)–C(4)	0.1326(6)
N(7)–C(3)	0.1354(6)	N(8)–C(4)	0.1454(6)
N(9)–N(10)	0.1354(6)	N(9)–C(5)	0.1366(6)
N(10)–C(6)	0.1305(6)	N(11)–C(6)	0.1336(6)
N(11)–C(5)	0.1343(6)	N(12)–C(6)	0.1457(6)

Table 3
Bond angles (°)

O(4)–YbO(1)	103.1(2)	O(4)–Yb–O(7)	89.61(14)
O(1)–Yb–O(7)	142.2(2)	O(4)–Yb–O(12)	172.9(2)
O(1)–Yb–O(12)	83.5(2)	O(7)–Yb–O(12)	86.5(2)
O(4)–Yb–O(13)	86.1(2)	O(1)–Yb–O(13)	72.5(2)
O(7)–Yb–O(13)	73.0(2)	O(12)–Yb–O(13)	98.5(2)
O(4)–Yb–O(10)	83.8(2)	O(1)–Yb–O(10)	75.2(2)
O(7)–Yb–O(10)	142.2(2)	O(12)–Yb–O(10)	95.6(2)
O(13)–Yb–O(10)	142.9(2)	O(4)–Yb–O(11)	89.0(2)
O(1)–Yb–O(11)	140.8(2)	O(7)–Yb–O(11)	73.5(2)
O(12)–Yb–O(11)	84.1(2)	O(13)–Yb–O(11)	146.2(2)
O(10)–Yb–O(11)	69.3(2)	C(1)–O(1)–Yb	143.6(4)
C(3)–O(4)–Yb	140.7(3)	C(5)–O(7)–Yb	151.1(4)
C(1)–N(1)–N(2)	110.5(5)	C(2)–N(2)–N(1)	100.1(4)
C(2)–N(3)–C(1)	102.1(4)	O(3)–N(4)–O(2)	124.5(6)
O(3)–N(4)–C(2)	117.9(5)	O(2)–N(4)–C(2)	117.5(5)
C(3)–N(5)–N(6)	111.3(4)	C(4)–N(6)–N(5)	100.1(4)
C(4)–N(7)–C(3)	101.9(4)	O(6)–N(8)–O(5)	125.3(5)
O(6)–N(8)–C(4)	117.9(5)	O(5)–N(8)–C(4)	116.8(4)
N(10)–N(9)–C(5)	110.9(4)	C(6)–N(10)–N(9)	100.2(4)
C(6)–N(11)–C(5)	101.5(4)	O(8)–N(12)–O(9)	125.0(5)
O(8)–N(12)–C(6)	116.6(4)	O(9)–N(12)–C(6)	118.4(5)
O(1)–C(1)–N(3)	129.2(5)	O(1)–C(1)–N(1)	122.5(6)
N(3)–C(1)–N(1)	108.3(5)	N(2)–C(2)–N(3)	118.9(5)
N(2)–C(2)–N(4)	119.6(5)	N(3)–C(2)–N(4)	121.5(5)
O(4)–C(3)–N(5)	125.2(5)	O(4)–C(3)–N(7)	126.3(4)
N(5)–C(3)–N(7)	108.5(4)	N(6)–C(4)–N(7)	118.3(4)
N(6)–C(4)–N(8)	119.0(4)	N(7)–C(4)–N(8)	122.8(5)
O(7)–C(5)–N(11)	126.7(5)	O(7)–C(5)–N(9)	124.9(4)
N(11)–C(5)–N(9)	108.4(4)	N(10)–C(6)–N(11)	118.9(4)
N(10)–C(6)–N(12)	119.5(4)	N(11)–C(6)–N(12)	121.6(4)

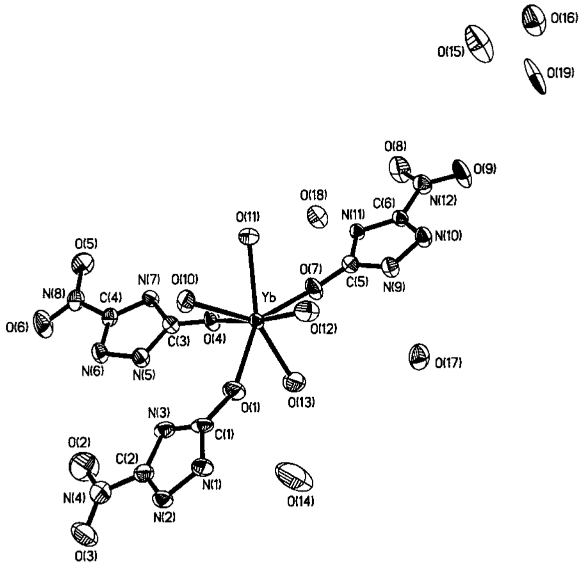

Fig. 1. Molecular structure of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$.

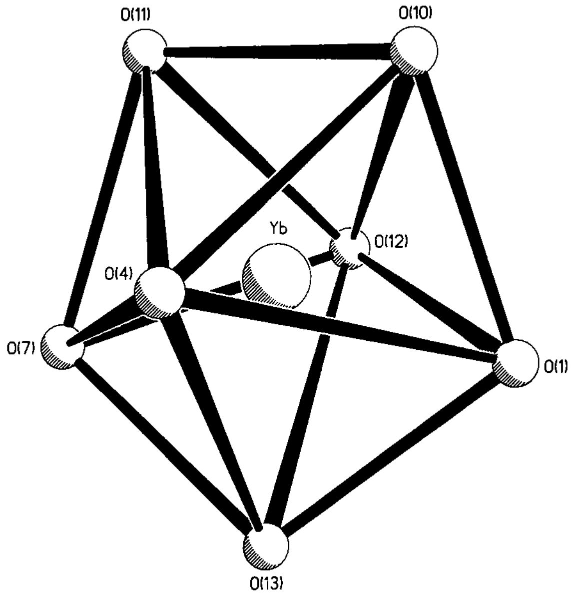

Fig. 3. Coordination polyhedron of Yb^{3+} in $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$.

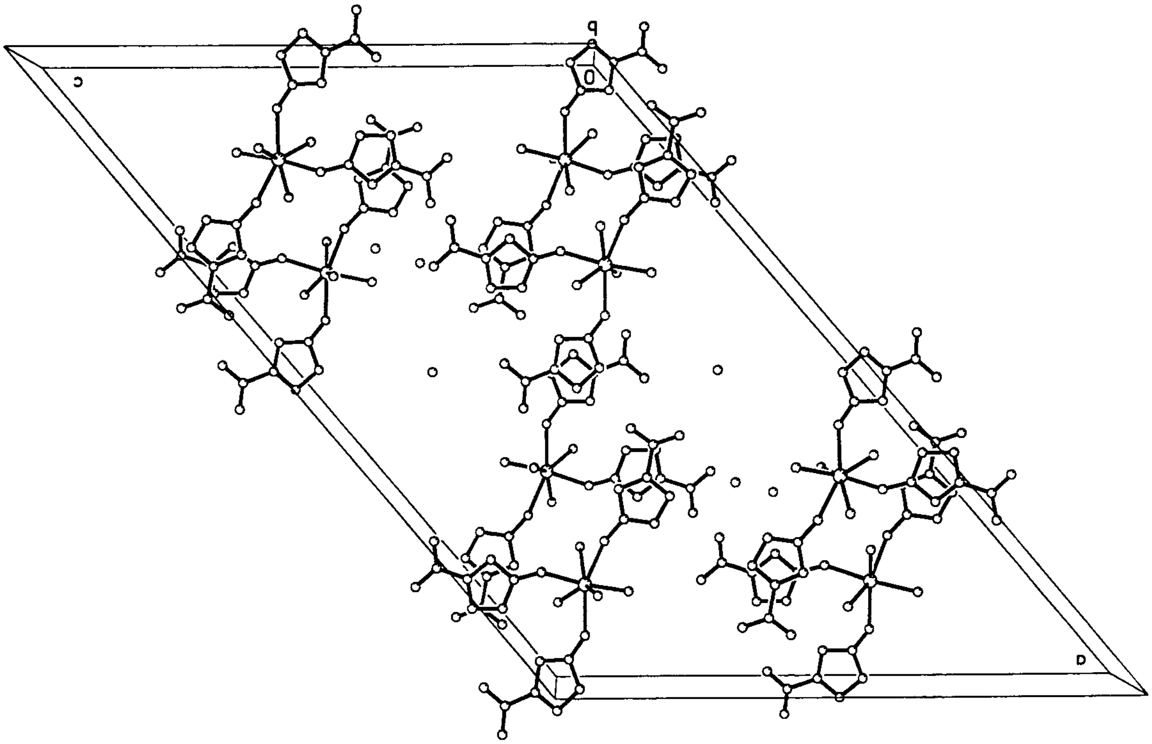

Fig. 2. Packing of the molecule $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ in the crystal lattice.

According to the calculation, the equations of the planes of three NTO anions are as follows:

$$-1.069x + 6.420y - 4.861z = -1.6074 \tag{1}$$

$$-6.454x + 6.570y + 1.898z = -1.2099 \tag{2}$$

$$1.706x + 6.666y - 1.809z = 2.0134 \tag{3}$$

The dihedral angles between planes (1) and (2), (1) and (3), (2) and (3) are 15.3°, 13.7° and 12.7°.

Table 4
Atomic coordinated and thermal parameters ($\times 10^3$, in nm^2)

Atoms	x	y	z	U_{eq}
Sr	0.1467(1)	0.5539(1)	0.6825(1)	0.23(1)
C(1)	−0.0475(4)	0.6350(2)	0.9654(7)	0.27(1)
C(2)	−0.2291(4)	0.6676(2)	0.9072(7)	0.24(1)
C(3)	0.1405(4)	0.3873(2)	0.5559(6)	0.23(1)
C(4)	0.3205(4)	0.4213(2)	0.6408(7)	0.25(1)
O(1)	0.0487(3)	0.6036(1)	0.9930(5)	0.32(1)
O(2)	−0.4189(3)	0.6227(1)	0.8301(6)	0.53(1)
O(3)	−0.4129(3)	0.7177(1)	0.8541(7)	0.69(1)
O(4)	0.0262(2)	0.3789(1)	0.5016(5)	0.30(1)
O(5)	0.3941(3)	0.5149(1)	0.6853(6)	0.49(1)
O(6)	0.5264(3)	0.4439(1)	0.7440(6)	0.56(1)
O(7)	0.0393(2)	0.5126(1)	0.2789(4)	0.27(1)
O(8)	0.3094(3)	0.6332(2)	0.8574(7)	0.53(1)
O(9)	0.2417(3)	0.4995(1)	1.0440(5)	0.34(1)
O(10)	0.2258(3)	0.6120(2)	0.3840(6)	0.55(1)
O(11)	0.4072(3)	0.6865(2)	0.2764(7)	0.74(1)
O(12)	0.1502(4)	0.7711(2)	1.0488(8)	1.13(2)
N(1)	0.0472(3)	0.6954(2)	0.9706(6)	0.33(1)
N(2)	−0.1659(3)	0.7167(1)	0.9325(6)	0.34(1)
N(3)	−0.1671(3)	0.6167(1)	0.9242(5)	0.26(1)
N(4)	−0.3631(3)	0.6698(2)	0.8596(6)	0.38(1)
N(5)	0.2272(3)	0.3429(1)	0.5908(6)	0.26(1)
N(6)	0.3455(3)	0.3646(1)	0.6457(6)	0.28(1)
N(7)	0.2033(3)	0.4392(1)	0.5900(5)	0.23(1)
N(8)	0.4215(3)	0.4627(1)	0.6938(6)	0.34(1)
H(7A)	0.0109(2)	0.5453(1)	0.1830(4)	0.32
H(7B)	0.0991(2)	0.4902(1)	0.2192(4)	0.32
H(8A)	0.3110(79)	0.6684(35)	0.9524(164)	3.78(79)
H(8B)	0.3743(31)	0.6265(20)	0.8302(71)	0.42(17)
H(9A)	0.3140(31)	0.5076(16)	1.1293(67)	0.56(16)
H(9B)	0.2266(33)	0.4618(13)	1.0372(65)	0.44(14)
H(10A)	0.2866(40)	0.6410(2)	0.3742(89)	1.24(26)
H(10B)	0.0329(57)	0.7230(34)	1.0135(167)	2.71(47)
H(N5)	0.2110(33)	0.3052(12)	0.5856(61)	0.28(12)

3.2. Crystal structure of [$Sr(NTO)_2(H_2O)_4$]$\cdot 2H_2O$

The crystal structure was found to be monoclinic, which belongs to space group $P2_1/c$ with crystallographic parameters of $a = 1.1034(1)$ nm, $b = 2.2742(2)$ nm, $c = 0.63398(9)$ nm, $\beta = 101.798(13)^\circ$, $V = 1.5573(4) nm^3$, $Z = 4$, $D_c = 1.936$ g cm^{-3}, $\mu = 35.45$ cm^{-1}, and $F(000) = 912$. The final $R = 0.0347$.

The atom coordinates, thermal parameters, bond lengths and bond angles are summarized in Tables 4–6. The molecular structure and atom labelling are shown in Fig. 4, the packing of the molecule in the crystal lattice and the coordination polyhedron of Sr^{2+} are illustrated in Figs. 5 and 6.

The results indicate that there is a symmetry centre in the molecular structure. The oxygen atoms [O(7), O(7A), O(8), O(9), O(10)] of the five water molecules, the N(7) and O(5) atoms in the NTO(2) ring, the O(4A) atom in the NTO(2A) ring and the O(1) atom in the NTO(1) ring are coordinated to the centre Sr. The oxygen atoms [O(7), O(7A), O(8A) O(9A), O(10A)] of five water molecules, the N(7A) and O(5A) atoms in the NTO (2A) ring, the O(4) atom in the NTO(2) ring and the O(1A) atom in the NTO (1A) ring are coordinated to another centre SrA. The coordinated bond lengths are in the 0.2535–0.2867 nm range and all of these are typical coordinated bond lengths. The O(7), O(7A), NTO(2A) and NTO(2) formed bridges between Sr and SrA. The distance

Table 5
Bond distances (in nm)

Sr–O(4A)	0.2535(3)	Sr–O(10)	0.2601(3)
Sr–O(7A)	0.2602(2)	Sr–O(8)	0.2625(3)
Sr–O(9)	0.2627(3)	Sr–O(1)	0.2682(3)
Sr–O(7)	0.2756(3)	Sr–N(7)	0.2774(3)
Sr–O(5)	0.2867(3)	Sr–SrA	0.43349(9)
C(1)–O(1)	0.1260(4)	C(1)–N(3)	0.1357(5)
C(1)–N(1)	0.1375(5)	C(2)–N(2)	0.1309(5)
C(2)–N(3)	0.1337(5)	C(2)–N(4)	0.1448(5)
C(3)–O(4)	0.1252(4)	C(3)–N(7)	0.1363(5)
C(3)–N(5)	0.1377(5)	C(4)–N(6)	0.1317(4)
C(4)–N(7)	0.1330(5)	C(4)–N(8)	0.1446(5)
O(2)–N(4)	0.1232(4)	O(3)–N(4)	0.1216(4)
O(4)–SrA	0.2535(3)	O(5)–N(8)	0.1223(4)
O(6)–N(8)	0.1214(4)	O(7)–SrA	0.2602(2)
N(1)–N(2)	0.1371(5)	N(5)–N(6)	0.1371(4)

Table 6
Bond angles (°)

O(4A)–Sr–O(10)	72.06(11)	O(4A)–Sr–O(7A)	81.93(8)
O(10)–Sr–O(7A)	138.80(11)	O(4A)–Sr–O(8)	99.56(11)
O(10)–Sr–O(8)	69.89(13)	O(7A)–Sr–O(8)	147.63(11)
O(4A)–Sr–O(9)	144.52(10)	O(10)–Sr–O(0)	137.78(11)
O(7A)–Sr–O(9)	79.97(9)	O(8)–Sr–O(9)	80.72(11)
O(4A)–Sr–O(1)	72.86(9)	O(10)–Sr–O(1)	124.46(11)
O(7A)–Sr–O(1)	74.45(8)	O(8)–Sr–O(1)	75.17(12)
O(9)–Sr–O(1)	72.99(9)	O(4A)–Sr–O(7)	68.75(8)
O(10)–Sr–O(7)	69.02(10)	O(7A)–Sr–O(7)	72.01(9)
O(8)–Sr–O(7)	138.89(11)	O(9)–Sr–O(7)	131.96(99)
O(1)–Sr–O(7)	131.58(8)	O(4A)–Sr–N(7)	130.57(9)
O(10)–Sr–N(7)	101.55(11)	O(7A)–Sr–N(7)	71.86(8)
O(8)–Sr–N(7)	124.85(11)	O(9)–Sr–N(7)	70.98(9)
O(1)–Sr–N(7)	133.93(9)	O(7)–Sr–N(7)	63.62(8)
O(4A)–Sr–O(5)	144.64(9)	O(10)–Sr–O(5)	72.60(11)
O(7A)–Sr–O(5)	125.99(8)	O(8)–Sr–O(5)	69.03(11)
O(9)–Sr–O(5)	68.83(10)	O(1)–Sr–O(5)	130.73(10)
O(7)–Sr–O(5)	97.37(9)	N(7)–Sr–O(5)	56.95(8)
O(4A)–Sr–SrA	71.66(6)	O(10)–Sr–SrA	102.95(9)
O(7A)–Sr–SrA	37.20(6)	O(8)–Sr–SrA	170.37(9)
O(9)–Sr–SrA	108.69(7)	O(1)–Sr–SrA	105.13(6)
O(7)–Sr–SrA	34.81(5)	N(7)–Sr–SrA	62.01(6)
O(5)–Sr–SrA	115.74(6)	O(1)–C(1)–N(3)	127.7(4)
O(1)–C(1)–N(1)	124.4(4)	N(3)–C(1)–N(1)	108.0(4)
N(2)–C(2)–N(3)	118.6(4)	N(2)–C(2)–N(4)	119.4(4)
N(3)–C(2)–N(4)	122.0(4)	O(4)–C(3)–N(7)	128.8(4)
O(4)–C(3)–N(5)	124.1(4)	N(7)–C(3)–N(5)	107.1(3)
N(6)–C(4)–N(7)	119.6(3)	N(6)–C(4)–N(8)	119.0(4)
N(7)–C(4)–N(8)	121.5(3)	C(1)–O(1)–Sr	126.2(3)
C(3)–O(4)–SrA	131.0(3)	N(8)–O(5)–Sr	121.9(2)
SrA–O(7)–Sr	107.99(9)	N(2)–N(1)–C(1)	110.5(3)
C(2)–N(2)–N(1)	100.7(3)	C(2)–N(3)–C(1)	102.2(3)
O(3)–N(4)–O(2)	124.4(4)	O(3)–N(4)–C(2)	118.2(4)
O(2)–N(4)–C(2)	117.3(4)	N(6)–N(5)–C(3)	111.8(3)
C(4)–N(6)–N(5)	99.3(3)	C(4)–N(7)–C(3)	102.2(3)
C(4)–N(7)–Sr	119.1(2)	C(3)–N(7)–Sr	135.9(2)
O(6)–N(8)–O(5)	124.6(4)	O(6)–N(8)–C(4)	118.7(3)
O(5)–N(8)–C(4)	116.7(3)		

from Sr to SrA is 0.4335 nm, and the angle of Sr–O(7)–SrA is 108.0°.

According to the calculation, the equations of the planes of NTO rings and Sr SrA O(7) O(7A) are as follows:

$$\mathrm{NTO(1)}: 2.185x - 0.892y + 6.335z = 5.6461 \qquad (4)$$

$$\mathrm{NTO(2)}: 2.948x - 0.670y + 6.324z = 2.8355 \qquad (5)$$

$$\mathrm{SrSrAO(7)O(7A)}: 6.497x + 18.092y - 0.123z = 8.9846 \qquad (6)$$

The dihedral angles between planes (4) and (5), (4) and (6), (5) and (6) are 4.1°, 93.1° and 90.2°.

3.3. Mechanism of thermal decomposition of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$

The DTA and TG curves for $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ are shown in Fig. 7. The DTA curve shows that there are two endothermic and two exothermic processes at temperatures >54.0°C.

The TG curve shows that the first mass loss is 14.7% between 54.0° and 104.8°C, which coincides with the calculated value (14.6%) of losing six water molecules from the complex. At the higher temperature, between 104.8° and 147.5°C, the mass loss is 24.2% which coincides with the calculated value (24.3%) of losing ten water molecules from the complex. Therefore, it was estimated that 10 water molecules were lost in two processes. The IR spectrum of the residue shows the absence of absorption peaks at 3407 cm^{-1} and 656 cm^{-1}, which denotes that the complex has been dehydrated.

Between 147.5° and 311.6°C, there is a rather severe mass loss. The IR spectrum of the residue at 320°C shows the absence of absorption peaks (for NO_2) at 1513 cm^{-1} and 1301 cm^{-1}, and the characteristic absorption peaks of $Yb_2(CO_3)_3$ and a polymer containing the –CO–NH-group being formed at 1525 and 835, 3394, 1533 and 1384 cm^{-1}, respectively. These observations show that the decomposition residue for this stage is a mixture. The amount of each component cannot be determined from the present experiments and it is impossible to determine the decomposition change stoichiometrically. The IR spectrum of the residue at 520°C shows that a strong absorption peak of Yb_2O_3 is formed at 572 cm^{-1}. At the end of this stage, the residue amounted to 26.0%. This value is in good agreement with the calculated loss of 26.6%.

On the basis of experimental and calculated results, the thermal decomposition mechanism of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ is postulated to be as follows:

$$\begin{aligned}&[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O}\\ &\quad\rightarrow [\mathrm{Yb(NTO)_3(H_2O)_4}] \rightarrow \mathrm{Yb(NTO)_3}\\ &\quad\rightarrow \mathrm{Yb_2(CO_3)_3} + \mathrm{polymer} \rightarrow \mathrm{Yb_2O_3}\end{aligned}$$

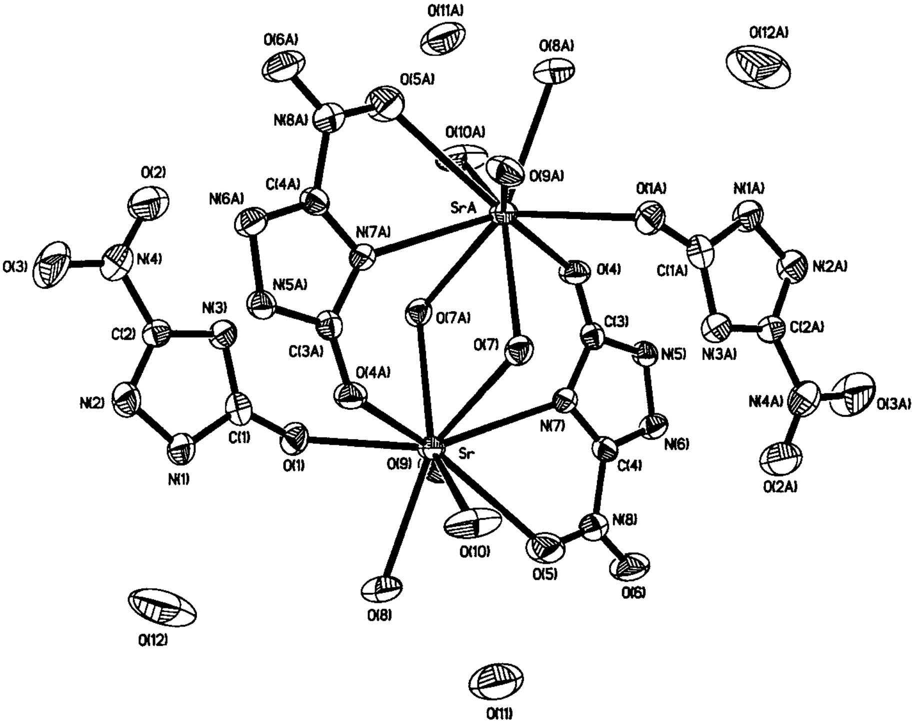

Fig. 4. Molecular structure of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$.

3.4. Mechanism of thermal decomposition of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$

The DSC and TG-DTG curves for $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ are shown in Fig. 8. The first stage of the decomposition process of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ appears as an endothermic peak between 75° and 158°C on the DSC curve. Otherwise, the TG-DTG curves show two mass loss processes. The first mass loss is 8.1% between 70° and 98°C, which coincides with the calculated value (7.9%) of losing two water molecules from the complex. The second mass loss is 24.2% between 98° and 162°C, which coincides with the calculated value (23.8%) of losing six water molecules from the complex. Therefore, it was estimated that the six water molecules were lost in two processes, the first involving loss of two water molecules and the second corresponding to the loss of the remaining four water. The IR spectrum of the residue shows the absence of absorption peaks at $3406\ cm^{-1}$ and $656\ cm^{-1}$, which denotes that the complex have been dehydrated.

The second stage of the decomposition process of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ appears as a relatively sharp peak between 25° and 355°C on the DSC curve, and the mass loss corresponding to the temperature range is 35.8%, as obtained from TG-DTG analyses. The IR spectrum of the residue at 360°C shows absorption bands at 2184 and $1178\ cm^{-1}$, which may be assigned to the compound $Sr(OCN)_2$, and at 1466 and $866\ cm^{-1}$ which may be assigned to $SrCO_3$. The absorption bands at 3406, 1634 and $1554\ cm^{-1}$ show that some kind of a polyamide exists in the residue, and the residue from decomposition is, therefore, a mixture.

The third stage of decomposition of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ shows a gradual exothermic peak between 429° and 510°C. The IR spectrum of the residue shows absorption bands only at 1457, 859 and $701\ cm^{-1}$, which coincide well with those in the standard spectrum of $SrCO_3$. The TG-DTG curves indicate that the mass loss corresponding to this temperature range is 10.8% and the residue comprises 32.2%, which agrees well with the theoretical value of

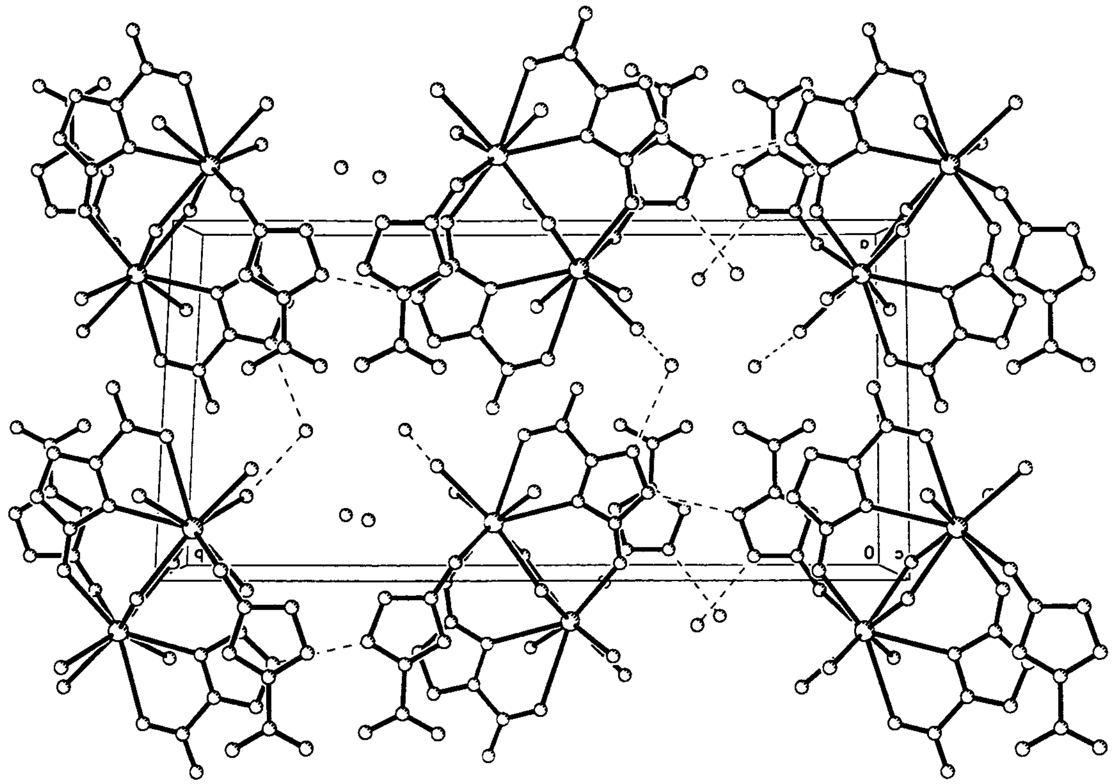

Fig. 5. Packing of the molecule $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ in the crystal lattice.

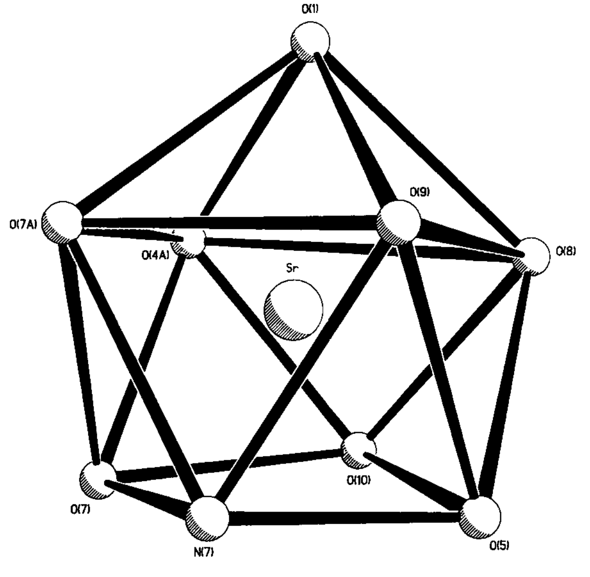

Fig. 6. Coordination polyhedron of Sr^{2+} in $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$.

32.5%. It could be concluded that the final decomposition residue of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ is strontium carbonate.

The experimental results confirm that the thermal decomposition mechanisms of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O$ can be expressed as:

$$\begin{aligned}&[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O\\&\rightarrow [Sr(NTO)_2(H_2O)_4] \rightarrow Sr(NTO)_2\\&\rightarrow SrCO_3 + Sr(OCN)_2 + \text{polyamides}\\&+\text{volatile substances} \rightarrow SrCO_3\end{aligned}$$

3.5. Enthalpy of an aqueous solution of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$

Results for the enthalpy of a solution of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$ in deionized water at 298.15 K are reported in Table 7, where $\Delta_{sol}H_m^{\theta}$ denotes the enthalpy of an aqueous solution of $[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O$, m the mass of $[Yb(NTO)_3(H_2O)_4]\cdot$

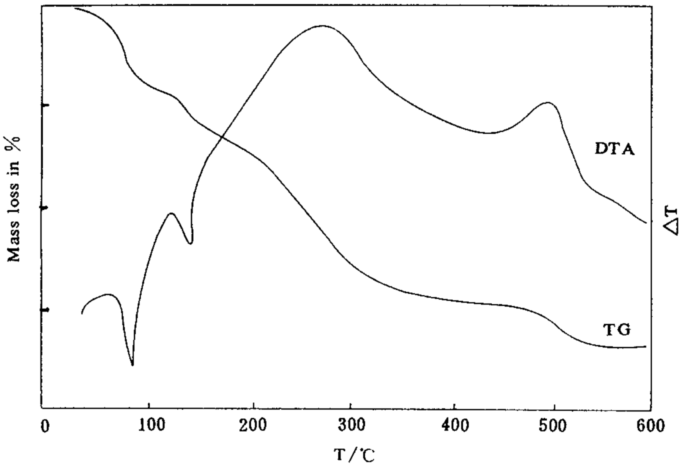

Fig. 7. DTA and TG curves for $[Yb(NTO)_3(H_2O)_4]{\cdot}6H_2O$ at a heating rate of 10°C min^{-1}.

Table 7
Enthalpy of aqueous solution of $[Yb(NTO)_3(H_2O)_4]{\cdot}6H_2O(cr)$ at 298.15 K

m/mg	r	$\Delta_{sol}H_m^\theta$/kJ mol^{-1}
3.01	109 212	37.44
5.10	64 747	37.64
5.11	63 329	37.92
7.10	46 613	37.11
8.11	40 625	37.77
9.01	45 683	37.82
11.10	29 746	38.10
		Mean 37.68 ± 0.46

$6H_2O$, and r the molar ratio $n(H_2O)/n\{[Yb(NTO)_3(H_2O)_4]{\cdot}6H_2O\}$.

Since $[Yb(NTO)_3(H_2O)_4]{\cdot}6H_2O$ is completely ionized in aqueous solution, its ionization process can be represented as

$$[Yb(NTO)_3(H_2O)_4]\cdot 6H_2O \overset{\Delta_{sol}H_m^\theta}{\longrightarrow} Yb^{3+}(aq,\infty) + 3NTO^-(aq,\infty) + 10H_2O(l) \quad (7)$$

In process (7), the greater values of r were used. Therefore, the mean of $\Delta_{sol}H_m^\theta$ in Table 7 can be considered at infinite dilution.

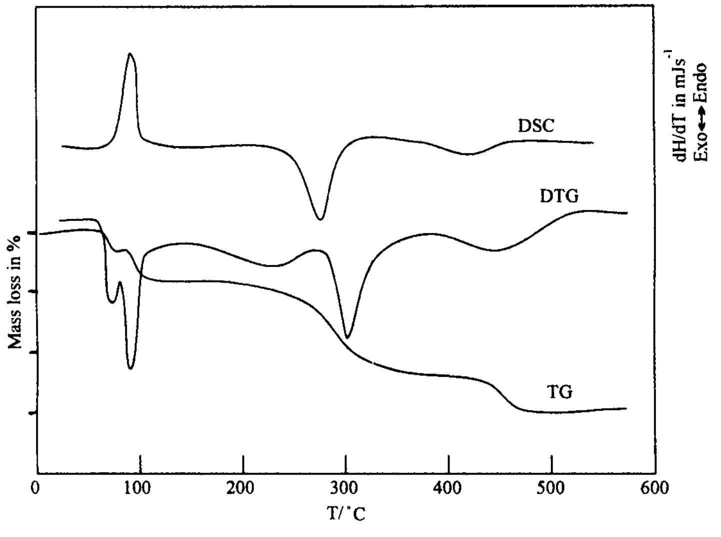

Fig. 8. DSC and TG-DTG curves for $[Sr(NTO)_2(H_2O)_4]{\cdot}2H_2O$ at a heating rate of 10°C min^{-1}.

3.6. Standard enthalpy of information of [Yb(NTO)$_3$-(H$_2$O)$_4$]·6H$_2$O(cr) $\Delta_f H_m^\theta$\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O, cr, 298.15 K\}

By substituting the mean of $\Delta_{\rm sol}H_m^\theta$ listed in Table 7 and the reported values of $\Delta_f H_m^\theta$ (Yb^{3+}, aq, ∞) = -674.4 kJ mol^{-1} [5], $\Delta_f H_m^\theta$ (NTO$^-$, aq, ∞) = $-(94.3 \pm 2.1)$ kJ mol^{-1} [6], and $\Delta_f H_m^0$ (H$_2$O, l) = -285.83 kJ mol^{-1} [5], into Eq. (2), we obtain

$$\begin{aligned}&\Delta_f H_m^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr, 298.15\,K}\}\\&\quad = \Delta_f H_m^\theta(\mathrm{Yb}^{3+},\mathrm{aq},\infty) + 3\Delta_f H_m^\infty(\mathrm{NTO}^-,\mathrm{aq},\infty)\\&\quad + 10\Delta_f H_m^\theta(\mathrm{H_2O},l) - \Delta_{\rm sol}H_m^\theta \qquad (8)\end{aligned}$$

the following values was obtained:

$$\begin{aligned}&\Delta_f H_m^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr, 298.15\,K}\}\\&\quad = -(3853.3 \pm 6.8)\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

3.7. Lattice enthalpy and energy of [Yb(NTO)$_3$-(H$_2$O)$_4$]·6H$_2$OΔH_L^θ\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O, cr\}, Δ_L^θ\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O,cr\}

Setting $\Delta H_{\rm L}^\theta$\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O,cr\} as the lattice enthalpy in forming the crystal [Yb(NTO)$_3$-(H$_2$O)$_4$]·6H$_2$O from Yb^{3+}(g), NTO$^-$(g) and H$_2$O (g) at 298.15 K, and $\Delta U_{\rm L}^\theta$\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O,cr\} as the crystal lattice energy.

$$\begin{aligned}&\mathrm{Yb^{3+}(g) + 3NTO^-(g) + 10H_2O(g)}\\&\quad \overset{\Delta H_{\rm L}^\theta}{\rightarrow} [\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O(cr)} \qquad (9)\end{aligned}$$

We have

$$\begin{aligned}&\Delta H_{\rm L}^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr}\}\\&\quad = \Delta_f H_m^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\\&\quad \cdot 6\mathrm{H_2O, cr, 298.15\,K}\} - \Delta_f H_m^\theta(\mathrm{Yb^{3+}, g})\\&\quad = 3\Delta_f H_m^\theta(\mathrm{NTO^-, g}) - 10\Delta_f H_m^\ominus(\mathrm{H_2O, g})\\&\qquad (10)\end{aligned}$$

and

$$\begin{aligned}&\Delta U_{\rm L}^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr}\}\\&\quad = \Delta H_{\rm L}^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr}\}\\&\quad - \Delta nRT \qquad (11)\end{aligned}$$

where $\Delta_f H_{\rm m}^0$ (Yb^{3+}, g) = 4318.9 kJ mol^{-1} [5], $\Delta_f H_{\rm m}^\theta$ (NTO$^-$, g) = -374.3 kJ mol^{-1} [7], $\Delta_f H_{\rm m}^\theta$ (H$_2$O, g) = -241.82 kJ mol^{-1} [5], $\Delta n = -14; RT = 2.5$ kJ mol^{-1}.

By substituting the above-mentioned data into Eqs. (10) and (11), the following values are obtained:

$$\begin{aligned}&\Delta H_{\rm L}^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr}\}\\&\quad = -4631\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}&\Delta U_{\rm L}^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr}\}\\&\quad = -4596\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

3.8. Standard enthalpy of dehydration of [Yb(NTO)$_3$-(H$_2$O)$_4$]·6H$_2$O(cr) ΔH_d^θ\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O, cr\}

According to process (12) and Eq. (13), namely

$$\begin{aligned}&[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O}\\&\quad \overset{\Delta H_{\rm d}^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O,cr}\}}{\longrightarrow} \mathrm{Yb(NTO)_3(cr)}\\&\quad + 10\mathrm{H_2O}(l) \qquad (12)\end{aligned}$$

and

$$\begin{aligned}&\Delta H_{\rm d}^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\cdot 6\mathrm{H_2O, cr}\}\\&\quad = \Delta_f H_m^\theta[\mathrm{Yb(NTO)_3, cr}] + 10\Delta_f H_m^\ominus(\mathrm{H_2O}, l)\\&\quad - \Delta_f H_m^\theta\{[\mathrm{Yb(NTO)_3(H_2O)_4}]\\&\quad \cdot 6\mathrm{H_2O, cr, 298.15\,K}\} \qquad (13)\end{aligned}$$

the value of $\Delta_f H_{\rm d}^\theta$\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O,cr, 298.15 K\} = 391 kJ mol^{-1} may be obtained from the value of $\Delta_f H_m^\theta$\{[Yb(NTO)$_3$(H$_2$O)$_4$]·6H$_2$O,cr, 298.15 K\} = -3853.3kJ mol^{-1}, obtained in this work, and the reported values ΔfH_m^θ[Yb(NTO)$_3$,cr,198.15 K] = -604.0 kJ mol^{-1} [7], $\Delta_f H_m^\theta$(H$_2$O,l) = -285.83 kJ mol^{-1} [5].

3.9. Enthalpy of solution in water of [Sr(NTO)$_2$(H$_2$O)$_4$]·2H$_2$O

The mean of the enthalpy of solution of [Sr(NTO)$_2$-(H$_2$O)$_4$]·2H$_2$O in deionized water at 298.15 K is 95.81 ± 0.53 kJ mol^{-1}. The molar ratio n(H$_2$O)/n-\{Sr(NTO)$_2$(H$_2$O)$_4$]·2H$_2$O\} lies in the 65 701–92 829 range. Therefore, the mean of $\Delta_{\rm sol}H_m^\theta$ can be considered at infinite dilution.

Since [Sr(NTO)$_2$(H$_2$O)$_4$]·2H$_2$O is completely ionized in aqueous solution, its ionization process can be represented as

$$[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O} \xrightarrow{\Delta_{\mathrm{sol}}H_m^\theta} \mathrm{Sr^{2+}(aq,\infty)} + 2\mathrm{NTO^-(aq,\infty)} + 6\mathrm{H_2O}(l) \qquad (14)$$

3.10. Standard enthalpy of formation of [Sr(NTO)$_2$-(H$_2$O)$_4$]·2H$_2$O$\Delta_f H_m^\theta${[Sr(NTO)$_2$(H$_2$O)$_4$]·2H$_2$O, cr, 298.15 K}

By substituting the mean of $\Delta_{\mathrm{sol}}H_m^\theta$ and the reported values of $\Delta_f H_m^\theta(\mathrm{Sr^{2+}},\mathrm{aq},\infty) = -545.8$ kJ mol^{-1} [5], $\Delta_f H_m^\theta(\mathrm{H_2O},\ \mathrm{l}) = -285.83$ kJ mol^{-1} [5], and $\Delta_f H_m^\theta$ ($\mathrm{NTO^-},\mathrm{aq},\infty) = -(94.3 \pm 2.1)$ kJ mol^{-1} [6], into Eq. (15),

$$\begin{aligned}&\Delta_f H_m^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O},\mathrm{cr},298.15\,\mathrm{K}\}\\&= \Delta_f H_m^\theta(\mathrm{Sr^{2+}},\mathrm{aq},\infty) + 2\Delta_f H_m^\theta(\mathrm{NTO^-},\mathrm{aq},\infty)\\&\quad + 6\Delta_f H_m^\theta(\mathrm{H_2O},l) - \Delta_{\mathrm{sol}}H_m^\theta \qquad (15)\end{aligned}$$

the following value was obtained:

$$\Delta_f H_m^\theta = -(2545.2 \pm 4.7)\,\mathrm{kJ\,mol^{-1}}$$

3.11. Lattice enthalpy and energy of [Sr(NTO)$_2$-(H$_2$O)$_4$]·2H$_2$O$\Delta H_{\mathrm{L}}^\theta${[Sr(NTO)$_2$(H$_2$O)$_4$·2H$_2$O, cr}, $\Delta U_{\mathrm{L}}^\theta${[Sr(NTO)$_2$(H$_2$O)$_4$]·2H$_2$O, cr}

Setting $\Delta H_{\mathrm{L}}^\theta$\{[Sr(NTO)$_2$(H$_2$O)$_4$·2H$_2$O,cr\} as the lattice enthalpy in forming the crystal [Sr(NTO)$_2$-(H$_2$O)$_4$]·2H$_2$O from Sr^{2+}(g), NTO$^-$(g) and H$_2$O(g) at 298.15 K, and $\Delta U_{\mathrm{L}}^\theta$\{[Sr(NTO)$_2$(H$_2$O)$_4$]·2H$_2$O,cr\} as the crystal lattice energy

$$\mathrm{Sr^{2+}(g)} + 2\mathrm{NTO^-(g)} + 6\mathrm{H_2O(g)} \xrightarrow{\Delta[\mathrm{Sr}H_{\mathrm{L}}^\theta} \mathrm{(NTO)_2(H_2O)_4]\cdot 2H_2O(cr)} \qquad (16)$$

we have

$$\begin{aligned}&\Delta H_l^\theta\{\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O},\mathrm{cr}\}\\&= \Delta_f H_m^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O},\mathrm{cr},298.15\,\mathrm{K}\}\\&\quad - \Delta_f H_m^\theta(\mathrm{Sr^{2+}},\mathrm{g}) - 2\Delta_f H_m^\theta(\mathrm{NTO^-},\mathrm{g})\\&\quad - 6\Delta_f H_m^\theta(\mathrm{H_2O},\mathrm{g}) \qquad (17)\end{aligned}$$

and

$$\begin{aligned}&\Delta[U_{\mathrm{L}}^\theta\{\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O},\mathrm{cr}\}\\&= \Delta H_{\mathrm{L}}^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O},\mathrm{cr}\}\\&\quad - \Delta nRT \qquad (18)\end{aligned}$$

where $\Delta_f H_m^0$ (Sr^{2+}, g) = 1790.6 kJ mol^{-1} [5]; $\Delta_f H_m^\theta$ (NTO$^-$, g) = −374.3 kJ mol^{-1} [7]; $\Delta_f H_m^\theta$ (H$_2$O,g) = −241.82 kJ mol^{-1} [5]; $\Delta n = -9$; $RT = 2.5$ kJ mol^{-1}.

By substituting the above-mentioned data into Eqs. (17) and (18), the following values are obtained:

$$\Delta H_{\mathrm{L}}^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O},\mathrm{cr}\} = -2136\,\mathrm{kJ\,mol^{-1}};$$

$$\Delta U_{\mathrm{L}}^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O},\mathrm{cr}\} = -2114\,\mathrm{kJ\,mol^{-1}};$$

3.12. Lattice energy and enthalpy of Sr (NTO)$_2$(cr), $\Delta U_{\mathrm{L}}^\theta$[Sr(NTO)$_2$,cr], ΔH_L^θ[Sr(NTO)$_2$,cr]

Values of $\Delta U_{\mathrm{L}}^\theta$[Sr(NTO)$_2$, cr] are calculated using Kapustinskii's equation [8]:

$$\Delta U_{\mathrm{L}}^\theta = 1201.6\frac{\eta_1\eta_2\sum n'}{\gamma_1+\gamma_2}\left(1-\frac{0.345}{\gamma_1+\gamma_2}\right)\mathrm{kJ\,mol^{-1}} \qquad (19)$$

where η_1 and η_2 are the moduli of the anion and cation charges, n' the number of ions in the molecule, γ_1 and γ_2 the radii of anion and cation, respectively, in Å. For Sr(NTO)$_2$(cr), $\eta_1 = \eta_{\mathrm{NTO}} = 1$, $\eta_2 = \eta_{\mathrm{Sr^{2+}}} = 2$, $n' = 3$, $\gamma_1 = \gamma(\mathrm{NTO^-},\mathrm{g}) = 2.5$ Å [9], $\gamma_2 = \gamma(\mathrm{Sr^{2+}},\mathrm{g}) = 1.13$ Å [10].

The result of the calculation are obtained as follows:

$$\Delta U_{\mathrm{L}}^\theta[\mathrm{Sr(NTO)_2},\mathrm{cr}] = -1797\,\mathrm{kJ\,mol^{-1}}$$

The $\Delta H_{\mathrm{L}}^\theta$[Sr(NTO)$_2$,cr] are calculated according to Eq. (20):

$$\Delta H_{\mathrm{L}}^\theta[\mathrm{Sr(NTO)_2},\mathrm{cr}] = \Delta U_{\mathrm{L}}^\theta[\mathrm{Sr(NTO)_2},\mathrm{cr}] + \Delta nRT \qquad (20)$$

where $\Delta n = -3$, $RT = 2.5$ kJ mol^{-1}.

The result of the calculation is obtained as follows:

$$\Delta H_{\mathrm{L}}^\theta[\mathrm{Sr(NTO)_2},\mathrm{cr}] = -1805\,\mathrm{kJ\,mol^{-1}}$$

3.13. Standard enthalpy of formation of Sr(NTO)$_2$(cr) $\Delta_f H_m^\theta$[Sr(NTO)$_2$, cr, 298.15 K]

The value of $\Delta_f H_m^\theta$[Sr(NTO)$_2$,cr,298.15 K] are calculated according to the process (21) and Eq. (22):

$$\mathrm{Sr^{2+}(g)} + 2\mathrm{NTO^-(g)} \xrightarrow{\Delta H_{\mathrm{L}}^\theta[\mathrm{Sr(NTO)_2,cr}]} \mathrm{Sr(NTO)_2(cr)} \qquad (21)$$

$$\Delta_f H_m^\theta[\mathrm{Sr(NTO)_2,cr}] = \Delta_f H_m^\theta(\mathrm{Sr^{2+},g}) + 2\Delta_f H_m^\theta(\mathrm{NTO^-,g}) + \Delta H_\mathrm{L}^\theta[\mathrm{Sr(NTO)_2,cr}] \quad (22)$$

where $\Delta_f H_m^\theta(\mathrm{Sr^{2+}},\ \mathrm{g}) = 1790.6\ \mathrm{kJ\,mol^{-1}}$; $\Delta_f H_m^\theta(\mathrm{NTO^-,g}) = -374.3\ \mathrm{kJ\,mol^{-1}}$; $\Delta H_\mathrm{L}^\theta[\mathrm{Sr(NTO)_2,cr}] = -1805\ \mathrm{kJ\,mol^{-1}}$.

By substituting the above-mentioned data into Eq. (22), the following value is obtained:

$$\Delta_f H_m^\theta[\mathrm{Sr(NTO)_2,cr}] = -763\,\mathrm{kJ\,mol^{-1}}$$

3.14. *Standard enthalpy of dehydration of $[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O(cr)\Delta H_d^\theta\{[Sr(NTO)_2(H_2O)_4]\cdot 2H_2O,cr\}$*

According to process (23) and Eq. (24)

$$[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O} \xrightarrow{\Delta H_\mathrm{d}^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O,cr}} \mathrm{Sr(NTO)_2(cr)} + 6\mathrm{H_2O}(l) \quad (23)$$

$$\Delta H_\mathrm{d}^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O,cr}\} = \Delta_f H_m^\theta[\mathrm{Sr(NTO)_2,cr}] + 6\Delta_\mathrm{f}\mathrm{H}_\mathrm{m}^\theta(\mathrm{H_2O,l}) - \Delta_f H_m^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O,cr,298.15\,K}\} \quad (24)$$

the value of $\Delta_f H_\mathrm{d}^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O,cr}\}$ of $67.2\ \mathrm{kJ\,mol^{-1}}$ may be obtained from the values of $\Delta_f H_m^\theta\{[\mathrm{Sr(NTO)_2(H_2O)_4}]\cdot 2\mathrm{H_2O,cr,298.15\ K}\}$ as $2545.2\ \mathrm{kJ\,mol^{-1}}$ and $\Delta_f H_m^\theta[\mathrm{Sr(NTO)_2,\ cr}]$ as $-763\ \mathrm{kJ\,mol^{-1}}$, obtained in this work, and the reported values $\Delta_f H_m^0(\mathrm{H_2O,\ l})$ as $-285.83\ \mathrm{kJ\,mol^{-1}}$.

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