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Thermochimica Acta 389 (2002) 43–47

thermochimica acta

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Preparation, crystal structure and thermodynamic properties of $[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$

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Received 13 November 2001; received in revised form 15 January 2002; accepted 15 January 2002

Abstract

$[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$ was prepared by adding magnesium carbonate hydroxide to the aqueous solution of 3-nitro-1,2,4-triazol-5-one (NTO). The single crystal structure has been determined by a four-circle X-ray diffractometer. The compound is monoclinic with space group $C2/c$ and unit-cell parameters $a = 2.3101(3)$ nm, $b = 0.6472(1)$ nm, $c = 1.4118(3)$ nm and $\beta = 124.05(1)^\circ$. From measurements of the enthalpy of solution in water at 298.15 K, the standard molar enthalpy of formation, lattice energy and lattice enthalpy have been determined as $-(3015.38 \pm 4.2)$ kJ mol^{-1}, -2680.7 and -2653.2 kJ mol^{-1}.

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

1. Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) is an explosive with 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 synthesis, properties and structure of its metal salts [4–8]. As a new high energy and low sensitivity energetic additive, NTO metal salts 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 paper, the authors prepared single crystals of $[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$, measured its structure and studied its thermodynamic properties.

2. Experimental

2.1. Experimental method

$[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$ was prepared as follows: a calculated amount of $Mg(OH)_2{\cdot}4MgCO_3{\cdot}6H_2O$ was

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0040-6031/02/$ – see front matter
PII: S0040-6031(02)00015-1

added gradually to the aqueous solution of NTO with stirring at 60 °C. A yellow precipitate was collected by filtration, washed with water and dried in vacuum drier. Single crystals suitable for X-ray measurement were obtained by recrystallization with distilled water at room temperature. Dimensions of the single crystal were 0.38 mm × 0.38 mm × 0.32 mm.

2.2. Experimental equipment and conditions

The elemental analyses were performed on a PE-2400 Elemental Analytical instrument (Perkin-Elmer, USA). The infrared spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets on a Bruker Eq Uninox-550 (Bruker, Germany) spectrometer. In the determination of the structure of the single crystal, X-ray intensities were recorded by a Siemens P4 automatic diffractometer using Mo Kα radiation (λ = 0.071073 nm) graphite monochromation. In the range of $2.13° < \theta < 26.00°$, 1664 independent reflections were obtained. The final conventional R_1 is 0.0279 and *wR* (unit weight) is 0.0749 for 1254 observable independent reflections with reflection intensity $I > 4\sigma(I)$. The hydrogen atom of N1 in NTO ring was obtained by geometric calculation after its existence was approved by difference Fourier synthesis, the hydrogen atoms of water molecules were made by difference Fourier synthesis. The structure of the compound was refined by full-matrix least-squares on F^2.

All measurements of the enthalpy of solution in deionized water were made using a microcalorimeter, type RD496-III (China, Southwest institutes of Electronic Engineering) and operated at 298.15 K. The experimental precision and accuracy of enthalpies of solution were frequently checked by measurement of the enthalpies of solution ($\Delta_{sol}H^{\theta}_{\infty}$) of crystalline KCl (NIST SRM1655) in deionized water at 298.15 K. The result $\Delta_{sol}H^{\theta}_{\infty} = 17.238 \pm 0.048$ kJ mol^{-1} is in excellent agreement with the recommended value reported in [10] (17.234 kJ mol^{-1}).

3. Results and discussion

3.1. Crystal structure

The analytical data of the compound are as follows: elemental analysis found (%)—C 11.20, H 4.21, N 26.22, calculated (%)—C 11.26, H 4.25, N 26.27. The characteristic peaks of IR are: $\nu^{s}_{N-H} = 3533.6\ cm^{-1}$, $\nu^{s}_{-OH} = 3414.1\ cm^{-1}$, $\nu^{s}_{C=O} = 1680.5\ cm^{-1}$, $\nu^{as}_{C-NO_2} = 1512.1\ cm^{-1}$, $\nu^{s}_{C-NO_2} = 1309.6\ cm^{-1}$.

The crystal structure was found to be monoclinic with space group *C*2/*c*. The complex could be expressed in the formula of $[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$ with unit-cell parameters $a = 2.3101(3)$ nm $b = 0.6472(1)$ nm $c = 1.4118(3)$ nm, $\beta = 124.05(1)°$, $F(0\,0\,0) = 888$, the unit-cell volume $V = 1.7489(5)$ nm^3, the molecule number in one unit-cell $Z = 4$, the absorption coefficient $\mu = 0.191\ mm^{-1}$, the calculated density $D_c = 1.620\ g/cm^3$.

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

The analytical results indicate that the molecule is centrosymmetrical. The Mg atom is located at the center of the symmetry. Six oxygen atoms of six water molecules are combined with a Mg atom to form $[Mg(H_2O)_6]^{2+}$. Two NTO anions and two crystalline water molecules are obtained by hydrogen bonds.

As shown in Table 2, the distances between Mg to O4–O6 are 0.2057(1), 0.2046(1) and 0.2087(1) nm and the bond angles of O5–Mg–O4, O4–Mg–O6 and O5–Mg–O6 are 88.37(5), 91.97(5) and 92.95(5)°, respectively. Therefore, the octahedron formed by the Mg atom and the six oxygen atoms of water is slightly deformed.

Table 1
Positional parameters and U_{eq} ($\times 10^2$, nm^2)

Atoms	*x*	*y*	*z*	U_{eq}
Mg	0.2500	0.7500	0	0.025(1)
O1	0.6910(1)	0.7483(2)	0.7353(1)	0.032(1)
O2	0.4069(1)	0.7455(2)	0.3735(1)	0.056(1)
O3	0.4798(1)	0.7500(2)	0.3246(1)	0.057(1)
O4	0.2395(1)	0.4719(2)	0.594(1)	0.038(1)
O5	0.2567(1)	0.8906(2)	0.1356(1)	0.038(1)
O6	0.3581(1)	0.7143(2)	0.884(1)	0.036(1)
O7	0.6194(1)	0.7359(2)	0.9192(1)	0.037(1)
N1	0.5777(1)	0.7560(2)	0.6898(1)	0.034(1)
N2	0.5113(1)	0.7560(2)	0.5942(1)	0.035(1)
N3	0.5905(1)	0.7480(2)	0.5470(1)	0.029(1)
N4	0.4659(1)	0.7490(2)	0.3960(1)	0.036(1)
C1	0.6259(1)	0.7504(2)	0.6627(1)	0.028(1)
C2	0.5242(1)	0.7510(2)	0.5155(1)	0.030(1)

Table 2
Selected bond lengths (nm)

Bond	Lengths	Bond	Lengths
Mg–O5A	0.2046(1)	N1–C1	0.1364(2)
Mg–O4A	0.2057(1)	N3–C2	0.1335(2)
Mg–O6	0.2087(2)	N4 –C2	0.1455(2)
O1–C1	0.1260(2)	Mg–O5	0.2046(1)
O3–N4	0.1219(2)	Mg–O4	0.2057(1)
Mg–O6A	0.2087(1)	O2–N4	0.1214(2)
N1–N2	0.1363(2)	N2–C2	0.1301(2)
N3–C1	0.1357(2)	N1–H1	0.0860(2)
H1–O7	0.1961(1)	N1 –O7	0.2818(2)
O4–H4A	0.0823(9)	H4A–O1B	0.1980(10)
O4–O1B	0.2792(2)	O4–H4B	0.0824(10)
H4B–O7B	0.1970(10)	O4–O7B	0.2793(2)
O5–H5A	0.0822(9)	H5A–O1C	0.1980(10)
O5–O1C	0.2798(2)	O5–H5B	0.0822(10)
H5B–O1D	0.1919(10)	O5–O1D	0.2736(2)
O6–H6B	0.0820(10)	H6B–O3	0.2124(11)
O6–O3	0.2929(2)	O6–H6A	0.0824(9)
H6A–N3B	0.1960(11)	O6– N3B	0.2767(2)
O7–H7B	0.0803(10)	H7B–O6B	0.2194(12)
O7– O6B	0.2972(2)	O7–H7A	0.0810(9)
H7A–N2B	0.2133(11)	O7– N2B	0.2920(2)

Symmetry transformations used to generate equivalent atoms. A: $-x+1/2,\ -y+3/2,\ -z$; O1B: $1-x,\ 1-y,\ 1-z$; O7B: $x-0.5,\ y-0.5,\ z-1$; O1C: $1-x,\ 2-y,\ 1-z$; O1D: $x-0.5,\ -y+1.5,\ z-0.5$; N3B: $1-x$, y, $0.5-z$; O6B: $1-x,\ 1-y,\ 1-z$; N2B: $1-x$, y, $1.5-z$.

Table 3
Selected bond angles (°)

Bond	Angles	Bond	Angles
O5A–Mg–O5	180.00(9)	O5A–Mg–O4A	88.37(5)
O5–Mg–O4A	91.63(5)	O5A–Mg–O4	91.63(5)
O5–Mg–O4	88.37(5)	O4A–Mg–O4	180.00(7)
O5A–Mg–O6	87.05(5)	O5–Mg–O6	92.95(5)
O4A–Mg–O6	88.03(5)	O4–Mg–O6	91.97(5)
O5A–Mg–O6A	92.95(5)	O5–Mg–O6A	87.05(5)
O4A–Mg–O6A	91.97(5)	O4–Mg–O6A	88.03(5)
O6–Mg–O6A	180.00(7)	N2–N1–C1	111.38(11)
C2–N2–N1	100.16(12)	C2–N3–C1	101.87(12)
O2–N4 –O3	124.17(14)	O2–N4 –C2	118.55(13)
O3–N4 –C2	117.27(13)	O1–C1–N3	128.25(13)
O1–C1–N1	124.17(13)	N3–C1–N1	107.58(12)
N2–C2–N3	119.00(13)	N2–C2–N4	118.99(13)
N3–C2–N4	122.02(13)	N1–H1–O7	172.6(1)
O4–H4A–O1B	169(2)	O4–H4B–O7B	176(2)
O5–H5A–O1C	167.8(19)	O5–H5B–O1D	172(2)
O6–H6B–O3	167.1(19)	O6–H6A–N3B	166(2)
O7–H7B–O6B	163(2)	O7–H7A–N2B	164.2(19)

According to the structure solution, the atoms of a NTO anion are nearly in a plane. The maximum deviation atom from the plane is O2 and the distance is 0.0033 nm, the mean deviation from the plane is 0.0013 nm. Because the two NTO anions are centrosymmetrical around the Mg atom, they are parallel. The triazolone mean bond has lengths of N1–N2, N3–C1, N1–C1 are 0.1363(2), 0.1357(2), 0.1364(2) nm, respectively. The bond length of carbonyl (C=O) is 0.1260(2) nm, is longer than the conventional carbonyl bond length (0.1210 nm), which indicates that the carbonyl oxygen is mixed up in the conjugation of the five-member ring.

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

The mean of the enthalpy of solution $[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$ in deionized water at 298.15 K is 73.29 ± 0.50 kJ mol^{-1}. The molar ratio $n(H_2O)/n\{[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O\}$ are 9385–14,811. Therefore, the mean of $\Delta_{sol}H^{\theta}_{m}$ can be considered at infinite dilution.

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

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

$$\begin{aligned}\Delta_{sol}H^{\theta}_{m} = {} & \Delta_f H^{\theta}_{m}(Mg^{2+}, aq, \infty) \\ & + 2\Delta_f H^{\theta}_{m}(NTO^{-}, aq, \infty) \\ & + 8\Delta_f H^{\theta}_{m}(H_2O, aq, \infty) \\ & - \Delta_f H^{\theta}_{m}\{[Mg(H_2O)_6](NTO)_2{}^{-} \cdot 2H_2O, \\ & \quad cr, 298.15\,K\}\end{aligned} \quad (2)$$

Table 4
Summary of the thermochemical data (kJ mol^{-1})

Substance	State	$\Delta_f H^{\theta}_{m}$ (298.15 K)
Mg^{2+}	aq	−466.85 [11]
NTO^{-}	aq	−(94.3 ± 2.1) [12]
H_2O	aq	−285.83 [11]
$[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$	cr	−(3015.38 ± 4.2)[a]
Mg^{2+}	g	2348.5 [11]
NTO^{-}	g	−374.3 [13]
H_2O	g	−241.82 [11]

[a] See text.

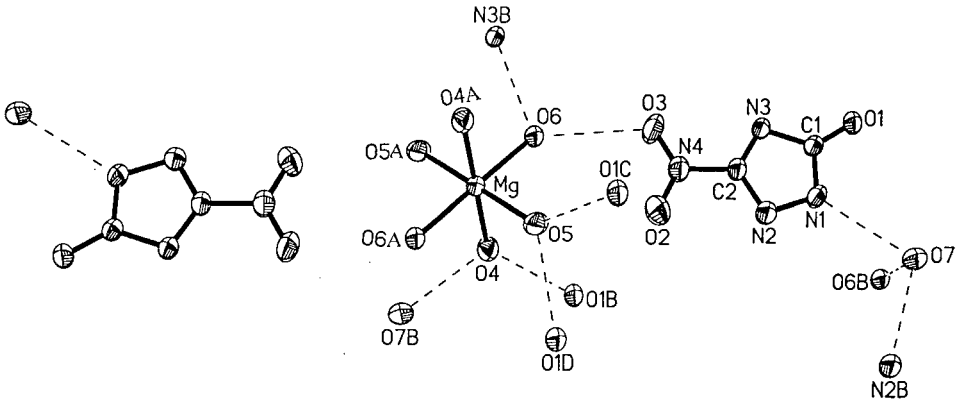

Fig. 1. Molecular structure of $[Mg(H_2O)_6](NTO)_2{\cdot}2H_2O$.

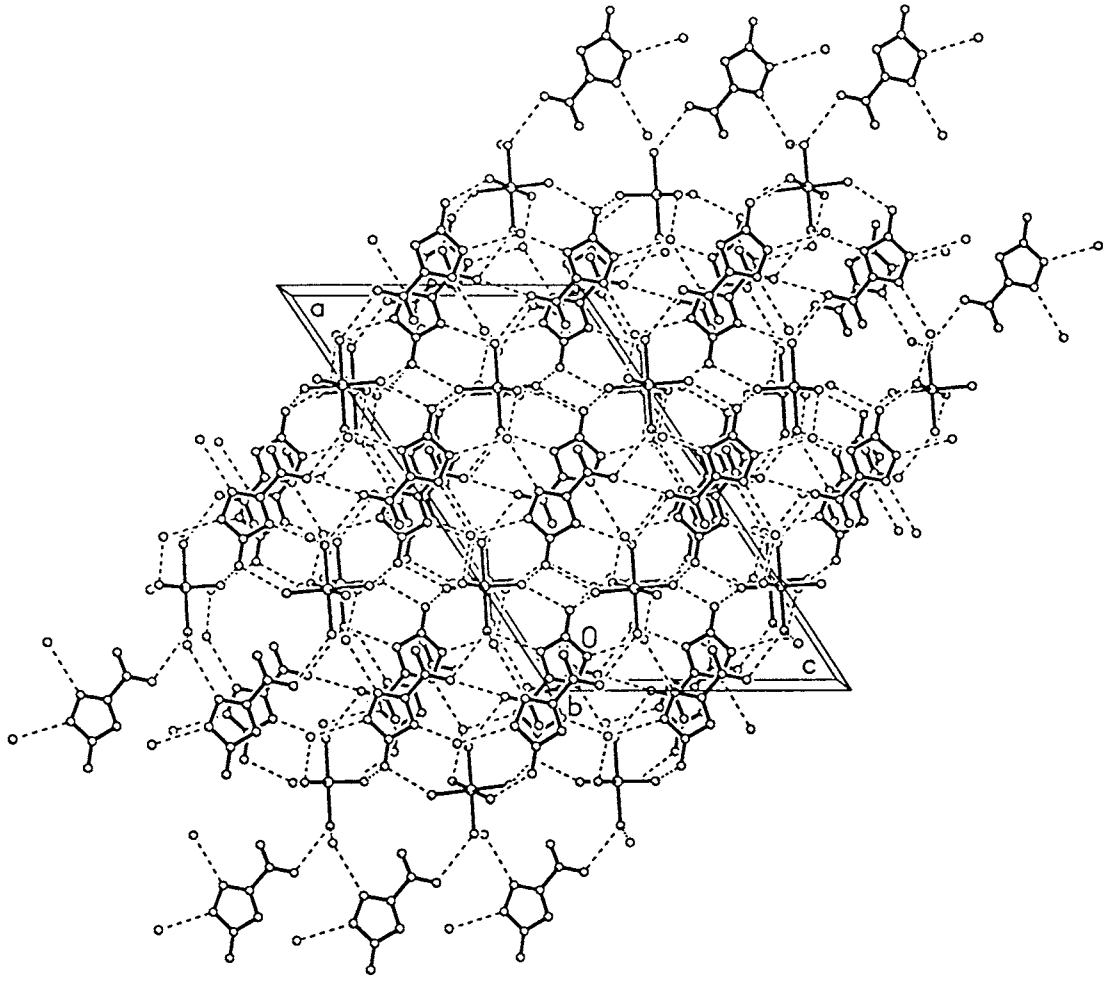

Fig. 2. The packing of the molecular in unit-cell.

Using the present data and data in Table 4, $\Delta_f H^\theta_m\{[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = -(3015.38 \pm 4.2)$ kJ mol^{-1}.

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

$$Mg^{2+}(g) + 2NTO^-(g) + 8H_2O(g) \overset{\Delta H^\theta_L}{\rightarrow} [Mg(H_2O)_6](NTO)_2 \cdot 2H_2O(cr) \quad (3)$$

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

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

Using the data in Table 4:

$$\Delta U^\theta_L\{[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = -2680.7\,kJ\,mol^{-1};$$

$$\Delta U^\theta_L\{[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O, cr\} = -2653.2\,kJ\,mol^{-1}$$

4. Conclusions

The single crystal structure of $[Mg(H_2O)_6](NTO)_2 \cdot 2H_2O$ was studied. The data suggest that six water molecules coordinate with a magnesium atom through the oxygen atom, two NTO anions are obtained by electrostatic action, two crystalline water molecules are obtained by hydrogen bonds. The crystal structure of $[Sr(NTO)_2(H_2O)_4] \cdot 2H_2O$ [6] is very different while $[Co(H_2O)_6](NTO)_2 \cdot 2H_2O$ [4] and $[Ni(H_2O)_6](NTO)_2 \cdot 2H_2O$ [14] is similar to the presently studied crystal. From the ion radius data: $r(Mg^{2+}) = 0.065$ nm, $r(Co^{2+}) = 0.074$ nm, $r(Ni^{2+}) = 0.072$ nm and $r(Sr^{2+}) = 0.113$ nm [15], we can see the structure of the NTO complexes have a definite relation with the ion radius.

Acknowledgements

We, the authors of the paper, gratefully acknowledge the National Science Foundation of China (Grant 29971025) for its financial support.

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