

3,5-二羟基-2,4,6-三硝基苯酚铷的晶体结构和热行为

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关键词: 3,5-二羟基-2,4,6-三硝基苯酚铷; 晶体结构; 热行为

中图分类号: O614.23*2

文献标识码: A

文章编号: 1001-4861(2006)10-1852-05

Crystal Structure and Thermal Behavior of Rubidium 3,5-dihydroxy-2,4,6-trinitrophenolate

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Abstract: A novel energetic coordination compound, rubidium 3,5-dihydroxy-2,4,6-trinitrophenolate ($[\text{Rb}(\text{DHTNP})]_n$), has been synthesized by reaction of trinitrophenol with Rb_2CO_3 in aqueous solution. Its crystal structure has been determined. The crystal belongs to monoclinic system with space group $C2/c$. In the crystal the Rb cation is coordinated to ten oxygen atoms from seven different DHTNP⁻ anions to form an irregular polyhedron. Two independent molecule geometry structures are found for DHTNP⁻ anion in the complex, which differ in benzene ring and their pattern of intramolecular hydrogen bonds. The DHTNP⁻ anion chains are interlaced with rubidium atoms as knots, and a three-dimensional infinite net structure is formed via coordination and hydrogen bonding. The hydrogen bond and cation-anion interactions are the predominant driving forces in the crystal packing. The thermal property of title complex was studied by using DSC and TG-DTG techniques. CCDC: 290623.

Key words: rubidium 3,5-dihydroxy-2,4,6-trinitrophenolate; crystal structure; thermal behavior

0 Introduction

Some nitrogen-rich alkaline and alkali-earth metals compounds of polynitro hydroxybenzenes can be used environmentally friendly primary explosives^[1-5]. 2,4,6-Trinitro-1,3,5-trihydroxybenzene (trinitrophenol, TNPG) belongs to a polynitro hydroxybenzene and has been used in chemical industry as an ingredi-

ent for priming composition, percussion caps and detonator formulations^[6]. Therefore, in recent years, it has been exploited to prepare a number of salts of based on alkali metals, alkaline earth metals, some transition metals and nitrogen-rich compounds used as energetic material. Several crystal structures of salts of TNPG with organic or metallic cations have been reported^[7-10]. But the heavy alkali metal salt, Rb-TNPG compound,

收稿日期: 2006-03-21。收修稿日期: 2006-06-26。

国家自然科学基金资助项目(No.20471008)和北京理工大学基础研究基金资助项目(No.BIT-UBF-200302B01; BIT-UBF-200502B4221)。

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has never been reported yet. In this work, mono-rubidium salt of TNPG (rubidium 3,5-dihydroxy-2,4,6-trinitrophenolate, $[\text{Rb}(\text{DHTNP})]_n$) has been synthesized by reaction of TNPG with Rb_2CO_3 in aqueous solution and a single crystal of the compound was cultivated. The crystal structure has been determined. Because of our interest in the coordination properties of 3,5-dihydroxy-2,4,6-trinitrophenolate anion and particular in its deformation in salts, we undertook the structure analysis of Rb-DHTNP. The thermal decomposition mechanism was studied preliminarily, which can expand the use of this kind compound.

1 Experimental

1.1 Materials and instruments

Rubidium carbonate (made in Jiangxi Lithium Factory, China) was heated in an electric furnace at 500 °C for 2 h, and then cooled, and put in a closed bottle. TNPG was synthesized according to the procedure reported in literature^[6], other reagents used for preparation of in synthesis Rb-TNPG were analytic grade.

Elemental analyses were performed on a Flash EA 1112 full-automatic trace element analyzer. The FTIR spectra were recorded on a Bruker Equinox 55 spectrometer (KBr pellets) in the range of 4 000~400 cm^{-1} . DSC and TG measurements were carried out using Perkin Elmer Pyris-1 differential scanning calorimeter and thermogravimetric balance, respec-

tively, using dry nitrogen as atmosphere with a pressure of 0.2 MPa.

1.2 Syntheses and crystal structure determination

Crystal of $[\text{Rb}(\text{DHTNP})]_n$ were prepared by reacting molar quantities of Rb carbonate and TNPG in distilled water and slow evaporation at room temperature. A yellow, rod-shaped crystal of dimensions of 0.40 mm \times 0.34 mm \times 0.22 mm was used for data collection. Anal. Found (calcd. %): C, 18.56 (18.32), H, 0.68 (0.51), N, 10.76 (10.69). All the experimental results are consistent with the calculated values. Therefore, its chemical formula can be written as $(\text{C}_6\text{H}_2\text{RbN}_3\text{O}_9)_n$. IR (cm^{-1} , KBr pellets): 3 441m ($\nu_{\text{O-H}}$), 1 640 s ($\nu_{\text{Ph-OH}}$), 1 480w ($\delta_{\text{C=C}}$), 1 347s (ν_{NO_2}), 1 196 s ($\nu_{\text{C-O}}$), 910 w, 785w, 711w (δ ring bone).

X-ray diffraction data (Table 1) were collected on a Siemens P4 full automatic four-circle diffractometer at 293 ± 2 K using graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073$ nm). Unit cell parameters were determined by least squares analysis. Empirical absorption correction was applied to the intensity data. The structure was solved by the direct methods and subsequent difference-Fourier map revealed the positions of the remaining atoms with the program SHELXS-97^[11]. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL 97^[12], and all hydrogen atoms were treated isotropically.

CCDC: 290623.

Table 1 Crystallographic data, data collection and structure refinement for $[\text{Rb}(\text{DHTNP})]_n$

Empirical formula	$\text{C}_6\text{H}_2\text{RbN}_3\text{O}_9$	Z	8
Formula weight	345.58	$D_c / (\text{Mg} \cdot \text{m}^{-3})$	2.384
Crystal size / mm	$0.40 \times 0.34 \times 0.22$	$F(000)$	1 344
T / K	293(2)	$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	5.124
Crystal system	Monoclinic	θ for data collection / ($^\circ$)	1.91~25.50
Space group	$C2/c$	h, k, l	0~11, 0~25, -11~11
Crystal color	Yellow	Reflns, collected / unique / observed	2 088 / 1 816 / 961
a / nm	0.939 5(1)	Data/restraints/parameters	1 816 / 2 / 185
b / nm	2.127 7(1)	Goodness-of-fit on F^2	0.936
c / nm	0.989 1(1)	Final R indices [$I > 2\sigma(I)$]	$R_1=0.034\,0$, $wR_2=0.048\,7^a$
$\beta / (^\circ)$	98.591(9)	R indices (all data)	$R_1=0.081\,9$, $wR_2=0.052\,2^a$
V / nm^3	1.954 92(30)	Largest difference peak and hole/ ($\text{e} \cdot \text{nm}^{-3}$)	419 and -403

^a $w=1/[\sigma^2(F_o^2) + (0.010\,6P)^2]$, where $P=(F_o^2 + 2F_c^2)/3$.

Symmetry operations: #1: $x+1, y, -z+1/2$; #2: $-x+1, -y+1, -z$; #3: $x-1/2, y+1/2, z$; #4: $-x, -y+1, -z+1$; #5: $x+1/2, y+1/2, z$; #6: $x, -y+1, z-1/2$.

lengths and torsional angles. The calculated results showed that two ring planes of DHTNP⁻-1 and DHTNP⁻-2 are not parallel and the angle of two rings is 6.77°. DHTNP⁻-2 has an average C-C bond length that is 0.001 43(7) nm shorter than that of DHTNP⁻-1 and average C-N and C-O bond lengths that are longer by 0.000 2(8) and 0.001 9(5) nm, respectively (Table 2). And angles of benzene ring are also different. We suggest that, based on observed averaged bond lengths, DHTNP⁻-2 has less of a “push-pull” interaction than DHTNP⁻-1. Each phenoxide oxygen atom is coordinated simultaneously with two Rb atoms, and each Rb atom is also coordinated with two phenoxide oxygen atoms. The bond distances of C(1)-O(1) and C(5)-O(6) are 0.122 0 and 0.124 6 nm, which is closed to the value of carbonyl double bond^[5]. The seven coordinated oxygen atoms of DHTNP⁻-1 are linked with six Rb atoms, but those of DHTNP⁻-2 are linked with eight Rb atoms. Three nitro groups of DHTNP⁻-1 are twisted out of the plane of the benzene ring, but only two nitro groups of DHTNP⁻-2 are twisted out of the plane of the benzene ring, which are probably acting as ligands and are hydrogen bond effects. The structure data indicate that conjugation, resonance and hydrogen bonding effects play important roles to determine the molecule geometries. Moreover, the steric effect also plays an important role to determine the deformation of the benzene ring and the distortion of nitro group.

The molecular packing of [Rb(DHTNP)]_n is shown in Fig.2. The DHTNP⁻ molecular chains are interlaced with rubidium atoms as knots, and a three-dimensional

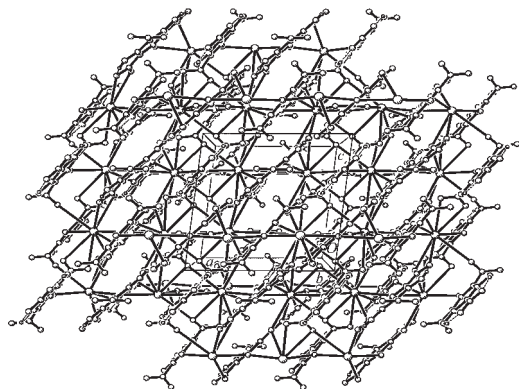


Fig.2 Packing arrangement of [Rb(DHTNP)]_n

infinite net structure is formed *via* coordination and hydrogen bonding. The coordinated Rb⁺ cations and the DHTNP⁻ anions are linked by electrostatic interactions, weak van der Waals' forces and intramolecular hydrogen bonds.

2.2 Thermal behavior

Fig.3 and Fig.4 show the DSC and TG-DTG curves of [Rb(DHTNP)]_n. In the DSC curve, there are two distinct exothermic peaks. The first one is an initial intense exothermic process with the peak temperature at 207.1 °C, which means that it is a very rapidly explosive decomposition process, and the second is other intense exothermic process with exothermic peak at 268.3 °C. The exothermic enthalpy change is 2 005.8 kJ·mol⁻¹ and 1 585.6 kJ·mol⁻¹, respectively.

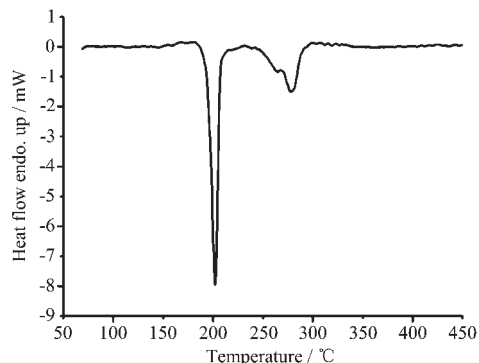


Fig.3 DSC curve of [Rb(DHTNP)]_n

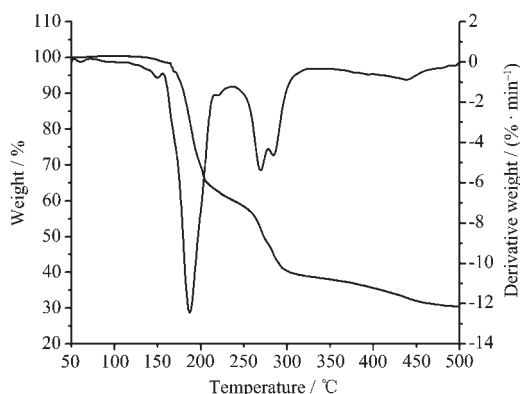


Fig.4 TG-DTG curves of [Rb(DHTNP)]_n

Corresponding to these two processes, there are two prominent and separated weight losses in TG curve. One occurs from 160.1 °C to 219.5 °C with the weight loss of 32.5% of the initial weight, another second weight loss of 19.9% occurs from 220.2 °C to 297.4 °C. It is shown that the above reaction product gives a large of heat with heating rate. Based on liter-

ature precedent^[3-5], the thermal decomposition mechanism of M-TNPG can be expected to proceed through the cleaving of three nitro-groups and a breakdown of benzene ring which can generate NCO^- and RCO_2^- in the solid residue, followed by the above residue decomposed and the final decomposed residue above 500 °C is 32.4% containing rubidium isonitrile^[4].

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