

Crystal Structure and Thermal Decomposition Mechanism of $[K(DNP)(H_2O)_{0.5}]_n$

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The new coordination polymer, $[K(DNP)(H_2O)_{0.5}]_n$ (DNP=2,4-dinitrophenol) was prepared by the reaction of 2,4-dinitrophenol with potassium hydroxide. The molecular structure was determined by X-ray single-crystal diffraction analysis, FT-IR techniques, and elemental analysis. The crystal is monoclinic, space group $C(2)/c$ with the empirical formula of $C_6H_4N_2O_5.5K$, $M_r=231.21$. The unit cell parameters are as follows: $a=2.0789(3)$ nm, $b=1.2311(2)$ nm, $c=0.7203(1)$ nm, $\beta=109.611(15)^\circ$, $V=1.7366(4)$ nm³, $Z=4$, $D_c=1.769$ g/cm³, $F(000)=936$, μ (Mo K α)=0.617 mm⁻¹. The potassium ions coordinate with all the oxygen atoms of phenolic hydroxyl group and nitro-group of different 2,4-dinitrophenol (DNP) ligands with high coordination number, and form a good cross-linked three-dimensional net structure of which makes the complex with good stabilities. The thermal decomposition of $[K(DNP)(H_2O)_{0.5}]_n$ has only an intense exothermic process in the temperature range of 338—343 °C corresponding to a mass loss of 75.02%. The final decomposition residue is potassium isocyanide.

Keywords dinitrophenol, potassium complex, crystal structure, thermal analysis

Introduction

As developing high-energy, low toxicity and environment friendly primary explosive has been becoming a new and important investigation field, much attention has been paid to nitrogen-rich potassium coordination compounds for the sake of their low toxicity and little pollutions.¹⁻¹¹ In order to make good use of potassium compounds, the reaction of 2,4-dinitrophenol (DNP) and potassium hydroxide was designed, and the title compound potassium 2,4-dinitrophenate (KDNP) was obtained. Its molecular structure and thermal decomposition mechanism were studied, and the relationship between its crystal structure and performance was discussed.

Experimental

Instruments and materials

The elemental analyses were performed on a Carlo Erba 1106 full-automatic trace organic element analyzer. IR spectrum was recorded on an EQUINOX55 infrared spectrometer. In the determination of the structure of the single crystal, X-ray intensities were recorded by a Siemens P4 full automatic four-circle diffractometer. The DSC experiment was carried out on a model

Pyris-1 differential scanning calorimeter with a heating rate of 10 °C/min, and flowing nitrogen gas was used as atmosphere with a flowing rate of 20 mL/min. The thermal decomposition process of KDNP was studied on a model Pyris-1 thermogravimeter analyzer with a heating rate of 10 °C/min, and nitrogen gas with a flowing rate of 20 mL/min was used as atmosphere.

2,4-Dinitrophenol (refined) and potassium hydroxide (analytical pure) were used in the synthesis of KDNP.

Synthesis and single crystal culture

DNP (5 g) was dissolved in ethanol (50 mL), and potassium hydroxide aqueous solution (50 mL) (4% in mass ratio) was gradually dropped into the DNP solution at 68 °C to get a clear buff solution until the pH reached 8—9, then kept for 15 min at the temperature. The reaction solution was naturally cooled to room temperature, and buff short needle crystals were precipitated. The precipitate was purified by a mixture solution of distilled water and ethanol. The final product was dried in oven. The yield was about 81%.

The above product was put into distilled water to get saturated solution. The filtered solution was kept in culturing dish in thermo-oven of 25 °C for 10 d to obtain the buff needle single-crystal for X-ray measurement. The results of analysis are: m.p. 323 °C; IR (KBr) ν :

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Received May 26, 2003; revised September 23; accepted October 6, 2003.
Project supported by the Foundation of BIT-UBF-200302B01.

3423, 3109, 1561, 1531, 1380, 1331, 920, 749 cm^{-1} .
Anal. calcd for $\text{C}_6\text{H}_4\text{N}_2\text{O}_{5.5}\text{K}$: C 31.17, H 1.73, N 12.12;
found C 31.56, H 1.57, N 11.91,

Determination of the structure of single crystal

Dimensions of the single crystal used for measurement were $0.40\text{ mm} \times 0.22\text{ mm} \times 0.20\text{ mm}$. X-ray diffraction intensities were recorded by a Siemens P4 full-automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071073\text{ nm}$). Cell parameters were determined from 25 reflections in the range of $3.30^\circ \leq \theta \leq 15.92^\circ$. Data were collected by ω scans at the temperature of 295(2) K. 1906 independent reflections were obtained, among which 1189 observed reflections with $I > 2\sigma(I)$ were used for the determination and refinement of the crystal structure in the range of $h=0-26$, $k=0-15$, $l=-9-8$. The crystal was monoclinic, space group $C(2)/c$ with the empirical formula of $\text{C}_6\text{H}_4\text{N}_2\text{O}_{5.5}\text{K}$. The cell parameters are: $a=2.0789(3)\text{ nm}$, $b=1.2311(2)\text{ nm}$, $c=0.7203(1)\text{ nm}$, $\beta=109.611(15)^\circ$, $V=1.7366(4)\text{ nm}^3$, $Z=4$, $D_c=1.769\text{ g/cm}^3$, $F(000)=936$, $M_r=231.21$.

The coordinates of K atom were obtained by direct method and those of the other non-hydrogen atoms were got by difference Fourier synthesis and subsequently refined anisotropically by full-matrix least-squares on F^2 methods. All hydrogen atoms were located at geometrical idealized position and refinement was performed by the mixed methods of full-matrix least-squares on F^2 isotropically and geometrically restraint. Final $R_1=0.0373$, $wR_2=0.0770$ [for data $I > 2\sigma(I)$], $R_1=0.0685$, $wR_2=0.0852$ (for all data), $s=0.894$, $\mu(\text{Mo } K\alpha)=0.617\text{ mm}^{-1}$, $w=1/[\sigma^2(F_o^2)+(0.0392P)^2]$, where $P=(F_o^2+2F_c^2)/3$. The final difference map: $(\Delta P)_{\text{max}}=183.0\text{ e}\cdot\text{nm}^{-3}$, $(\Delta P)_{\text{min}}=-195.0\text{ e}\cdot\text{nm}^{-3}$.

All calculations were carried out with SHELXTL97 program. The atom coordinates, thermal parameters, bond lengths and bond angles are summarized in Tables 1—3, respectively. The unit structure, the extended coordination scheme of potassium, the coordination polyhedrons of potassium in different states, and the packing of the molecule in crystal lattice are illustrated in Figures 1—5.

Results and discussion

Crystal structure of $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$

According to the results of elemental analysis and Figures 1 and 2, the molecular formula of the title compound is determined as $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$, and molecular weight is 231.21.

In $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$, K atom coordinates with O atoms of phenolic hydroxyl group and nitro-group, but K(1) and K(2) show different coordination numbers. K(1) coordinates with O(1), O(1A), O(2), O(2A), O(2B), O(2C), O(3B), O(3C), O(5E) and O(5D), where the coordination number is 10. The 10 coordination bonds are inversion-symmetrical distribution. Two steady-going aberrant six-membered rings and two aberrant four-

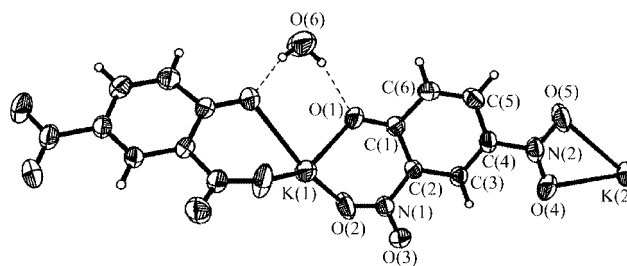


Figure 1 Unit structure of $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$.

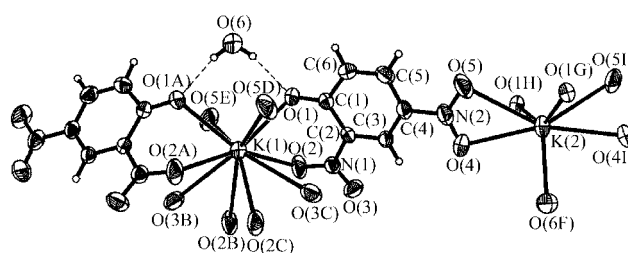


Figure 2 Extended coordination scheme of potassium ion in $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$.

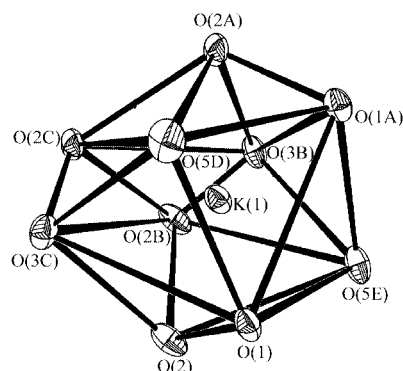


Figure 3 Coordination polyhedron of potassium ion (1) in $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$.

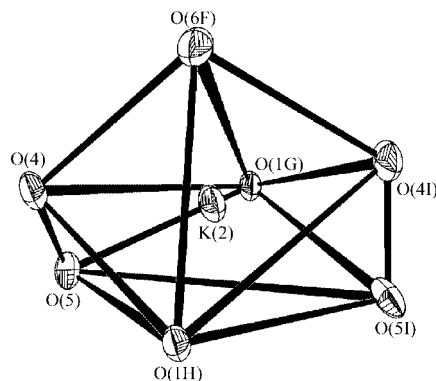


Figure 4 Coordination polyhedron of potassium ion (2) in $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$.

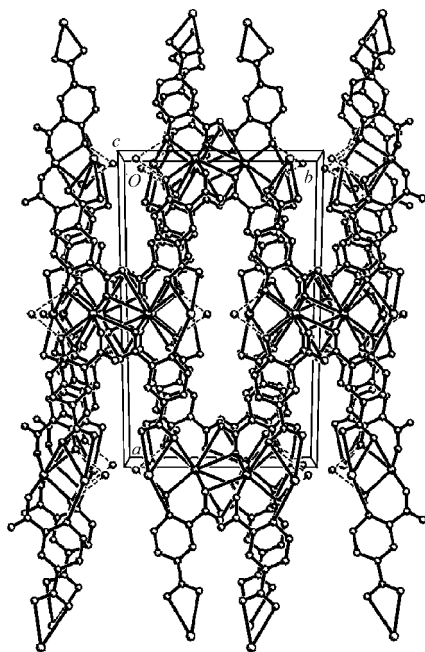


Figure 5 Packing arrangement of $[K(DNP)(H_2O)_{0.5}]_n$.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^5 \text{ nm}^2$) for the title compound

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
K(1)	0	3711(1)	2500	46(1)
K(2)	-5000	3537(1)	-7500	57(1)
O(1)	-743(1)	2234(1)	-305(3)	48(1)
O(2)	-568(1)	4245(2)	-1485(3)	61(1)
O(3)	-1399(1)	4971(1)	-3732(3)	54(1)
O(4)	-3677(1)	3934(2)	-4819(3)	69(1)
O(5)	-3909(1)	2335(2)	-4023(3)	65(1)
O(6)	0	672(3)	2500	82(1)
N(1)	-1170(1)	4255(2)	-2497(3)	36(1)
N(2)	-3494(1)	3061(2)	-4012(3)	47(1)
N(3)	3727(3)	6330(2)	3844(2)	24(1)
C(1)	-1366(1)	2437(2)	-1185(3)	35(1)
C(2)	-1623(1)	3424(2)	-2260(3)	31(1)
C(3)	-2316(1)	3617(2)	-3157(3)	33(1)
C(4)	-2776(1)	2846(2)	-3050(3)	36(1)
C(5)	-2562(1)	1855(2)	-2101(4)	43(1)
C(6)	-1888(1)	1665(2)	-1216(4)	43(1)

membered rings are formed. The bond lengths are between 0.27710—0.3185 nm, and the average bond length is 0.2966 nm. The lengths are a little longer than those of normal coordination bonds of transition metal

complexes,^{12,13} but similar to those of K—O of some crown ether coordinations.¹⁴

K(2) coordinates with O(1G), O(1H), O(4), O(4I), O(5), O(5I) and O(6F), and the 7 coordination bonds also have fine symmetry. The bond lengths are between 0.2628—0.3130 nm, and two four-membered rings are formed. The bond length of K(2)—O(6F) is 0.2628 nm, indicating that the water molecule in $[K(DNP)(H_2O)_{0.5}]_n$ is coordination water. In addition, the hydrogen bonds are formed between the two H atoms of the coordination water and O atoms of phenolic hydroxyl group of DNP. So the water can steadily lie in the polymer.

K shows a higher coordination number. This is because K atom is an alkali metal atom, and has a larger atomic radius, more coordination ligands are permitted to around it. On the other hand, K atom has less d electrons so it has less repulsive force to ligand, and the coordination atom easily bonds with the metal ion. All of the O atoms in DNP have lone-paired electrons so they are good coordination atoms, and DNP can serve as multidentate. Here, DNP is quadridentate ligand in $[K(DNP)(H_2O)_{0.5}]_n$.

As showed in Figure 5, one DNP can bond with three labeled K atoms with O atoms, and one K atom can coordinate with six or five DNP molecules, the infinite cross-linked three-dimensional network block is formed in the lattice. The coordination bonds of K—O of different molecules are staggeredly arranged like the brick form structures. These coordination bonds are co-actions, and have higher toughness. Therefore the coordination polymer of $[K(DNP)(H_2O)_{0.5}]_n$ is formed, and has high stability and good heat-resistant. The onset temperature of thermal decomposition process as shown in Figure 6 is 338 °C, which is the highest value in the common used energetic coordination compounds. When 20 mg of $[K(DNP)(H_2O)_{0.5}]_n$ was compacted to copper cap under the pressure of 39.2 MPa, and was hit by 2.0 kg drop hammer from 50 cm, the firing rate is zero. When 20 mg of $[K(DNP)(H_2O)_{0.5}]_n$ was compressed between two steel poles with mirror surfaces at the pressure of 1.96 MPa, and was hit horizontally with a 1 kg hammer from 90° angle, the firing rate is 40% only. All of these testing results confirm that the compound has very high stability.

Owing to the p-π conjugation between O(1) atom of phenolic hydroxyl group and benzene ring in $[K(DNP)(H_2O)_{0.5}]_n$, the electron cloud density of C(1) atom increases, and the electron cloud repulses the two electron pairs of sp² hybrid orbital, so the bond angles of C(2)-C(1)-C(6) is less than 120°. The experimental results approve such a theoretical hypothesis. The bond angle of C(2)-C(1)-C(6) is 114.1°. And the bond C(1)—O(1) has some double-bond character. The bond length is 0.1262 nm, of which is shorter than that of normal C—O (0.1430 nm) and close to that of natural double bond C=O (0.1220 nm).¹⁵

Because of the electrophilicity of nitro-group, the electron cloud density of the C atom linked with the

Table 2 Selected bond lengths (nm) for the title compound

K(1)—O(1)	0.27710 (18)	K(1)—O(1A)	0.27710 (18)	K(1)—O(2A)	0.27910 (18)
K(1)—O(2)	0.27910 (18)	K(1)—O(2B)	0.29725(19)	K(1)—O(2C)	0.29725(19)
K(1)—O(5D)	0.3111(2)	K(1)—O(5E)	0.3111(2)	K(1)—O(3B)	0.31846(18)
K(1)—O(3C)	0.31846(18)	K(2)—O(6F)	0.2628(3)	K(2)—O(1G)	0.27247(19)
K(2)—O(1H)	0.27247(19)	K(2)—O(4)	0.28224(18)	K(2)—O(4I)	0.28224(18)
K(2)—O(5I)	0.3130(2)	K(2)—O(5)	0.3130(2)	O(1)—K(2H)	0.27247(19)
O(2)—K(1B)	0.29725(19)	O(3)—K(1B)	0.31846(18)	O(5)—K(1D)	0.3111(2)
O(6)—K(2J)	0.2628(3)	O(2)—N(1)	0.1220(2)	O(3)—N(1)	0.1229(2)
O(1)—C(1)	0.1262(3)	O(4)—N(2)	0.1220(3)	N(2)—C(4)	0.1443(3)
C(1)—C(6)	0.1436(3)	N(1)—C(2)	0.1438(3)	C(1)—K(2H)	0.3494(2)
C(2)—C(3)	0.1389(3)	C(1)—C(2)	0.1443(3)	C(4)—C(5)	0.1396(3)
C(5)—C(6)	0.1352(3)	C(3)—C(4)	0.1367(3)	O(5)—N(2)	0.1240(3)

Table 3 Selected bond angles (°) for the title compound

O(1)-K(1)-O(1A)	97.96(7)	O(1)-K(1)-O(2A)	147.56(6)	O(1)-K(1)-O(2)	57.64(5)
O(2A)-K(1)-O(2)	152.79(9)	O(1)-K(1)-O(2B)	123.11(5)	O(1)-K(1)-O(2C)	124.39(5)
O(1A)-K(1)-O(2C)	123.11(5)	O(1A)-K(1)-O(2B)	124.39(5)	O(2A)-K(1)-O(2B)	89.32(4)
O(2)-K(1)-O(2B)	67.27(6)	O(2B)-K(1)-O(2C)	64.34(8)	O(1)-K(1)-O(5D)	72.03(5)
O(1A)-K(1)-O(5D)	76.40(6)	O(2A)-K(1)-O(5D)	80.87(6)	O(5D)-K(1)-O(5E)	131.07(8)
O(2)-K(1)-O(5D)	110.70(5)	O(2B)-K(1)-O(5D)	146.49(6)	O(2C)-K(1)-O(5D)	82.38(6)
O(6F)-K(2)-O(1G)	110.40(4)	O(6F)-K(2)-O(1H)	110.40(4)	O(1G)-K(2)-O(1H)	139.20(8)
O(6F)-K(2)-O(4)	80.03(5)	O(1G)-K(2)-O(4)	105.97(6)	O(1H)-K(2)-O(4)	81.12(6)
C(1)-O(1)-K(1)	117.59(1)	O(1)-C(1)-C(2)	121.30(2)	O(1)-C(1)-C(6)	124.60(2)
C(2)-C(1)-C(6)	114.10(2)	N(1)-O(2)-K(1)	127.70(1)	C(1)-C(2)-N(1)	121.62(2)
N(2)-O(4)-K(2)	104.46(1)	C(3)-C(2)-N(1)	116.20(2)	O(2)-N(1)-C(2)	120.20(2)
N(2)-O(5)-K(2)	88.83(1)	C(1)-C(2)-C(3)	122.20(2)	C(3)-C(4)-N(2)	118.40(2)
O(2)-N(1)-O(3)	120.70(2)	C(2)-C(3)-C(4)	119.50(2)	O(5)-N(2)-C(4)	118.40(2)
O(3)-N(1)-C(2)	119.14(2)	C(5)-C(4)-N(2)	120.20(2)	C(1)-C(6)-C(5)	123.40(2)
O(4)-N(2)-O(5)	121.80(2)	C(3)-C(4)-C(5)	121.30(2)	O(1)-C(1)-K(1)	43.97(1)
O(4)-N(2)-C(4)	119.80(2)	C(4)-C(5)-C(6)	119.40(2)		

Symmetry transformations used to generate equivalent atoms: A: $-x, y, -z+1/2$; B: $-x, -y+1, -z$; C: $x, -y+1, z+1/2$; D: $-x-1/2, -y+1/2, -z$; E: $x+1/2, -y+1$; F: $x-1/2, y+1/2, z-1$; G: $x-1/2, -y+1/2, z-1/2$; H: $-x-1/2, -y+1/2, -z-1$; I: $-x-1, y, -z-3/2$; J: $x+1/2, y-1/2, z+1$.

nitro-group decreases, the bond angle of C(1)-C(2)-C(3) should be more than 120°. The experimental result is 122.20°.

There are p- π conjugations and the π system in the benzene ring, so the molecular energy can keep a lower value, and this is benefit for the title molecule to keep stability.

The benzene ring in [K(DNP)(H₂O)_{0.5}]_n and the O atom of hydroxyl are coplanar, and the equation of the plane is: $-7.396x + 4.995y + 6.573z = 1.4461$. The mean deviation is 0.0013 nm.

The equation of the plane of which contains the o-nitro-group of the nitro-group near the hydroxyl, is:

$-9.566x + 6.923y + 5.774z = 2.6235$. The angle between this plane and the above plane is 14.0° due to the repulsion of electron cloud.

The equation of the plane of which contains the p-nitro-group of the hydroxyl, is: $-8.036x + 4.493y + 6.681z = 1.5026$. The angle between this plane and the benzene ring plane is 2.1°.

Thermal decomposition mechanism of [K(DNP)-(H₂O)_{0.5}]_n

The DSC and TG-DTG curves for [K(DNP)-(H₂O)_{0.5}]_n are shown in Figures 6 and 7. The DSC curve shows that there are two endothermic processes and one

intense exothermic process in the temperature range of 50 °C—450 °C. The first endothermic process is between 126—156 °C. TG curve shows that the mass loss is 3.63% corresponding to losing water molecule from $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$ in this temperature range, which coincides with the calculated value 3.89% very well. The IR spectrum of residue at 150 °C shows no absorption peak of H_2O at 3423 cm^{-1} , indicating that the first step of the thermal decomposition of $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$ is dehydration process. Because H_2O of $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$ is coordination water, the dehydration temperature is especially higher.^{16,17} The dehydration enthalpy is 34 kJ/mol.

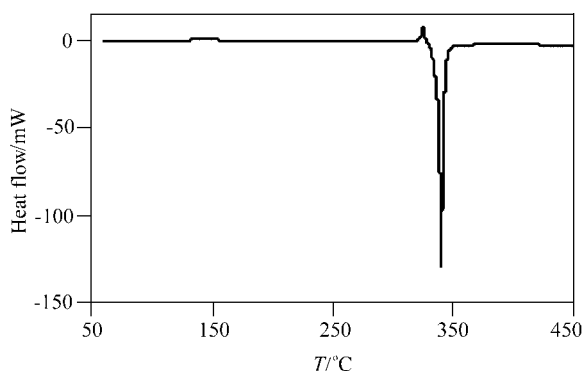


Figure 6 DSC curve of $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$.

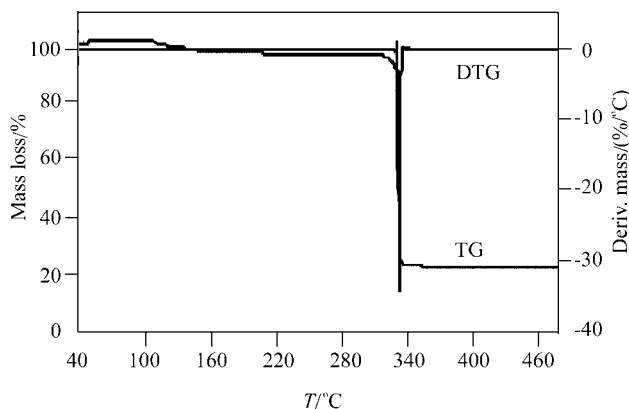


Figure 7 TG-DTG curves of $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$.

The further decomposition process occurs between 323 and 343 °C, and the exothermic decomposition enthalpy is 945 kJ/mol. There is an intense mass loss of 75.02% in the range of 323—355 °C on TG curve, corresponding to the exothermic process on DSC curve. The IR absorption band at 2163 cm^{-1} confirms the presence of KNC^{18} in the decomposed residues at 350 °C.

The thermal decomposition process of $[\text{K}(\text{DNP})-$

$(\text{H}_2\text{O})_{0.5}]_n$ is accomplished with only one exothermic step at the temperature as high as 323 °C and to give out a strong exothermic enthalpy. This is why the compound is widely used as an energetic material both in ammunition and civil applications.

On the basis of experimental and calculated results, the thermal decomposition of $[\text{K}(\text{DNP})(\text{H}_2\text{O})_{0.5}]_n$ is postulated to proceed as follows:



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