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Crystal Structure and Thermal Behavior of Potassium Dinitromethane

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Abstract: Potassium dinitromethane $\{K[CH(NO_2)_2]\}_n$ was synthesized. The single-crystal structure of $\{K[CH(NO_2)_2]\}_n$ was determined, which is triclinic, space group P-1 with crystal parameters of a=4.5285(11) Å, b=7.0377(17) Å, c=7.8543(19) Å, α =70.671(3)°, β = 88.557(3)°, γ = 75.818(4)°, V=228.58(10) ų, Z=2, D_c =2.094 g · cm⁻³, F(000)=144, S=1.060, μ (Mo K_α)=1.077 mm⁻¹, R_1 =0.0457, wR_2 =0.1399, $(\Delta p)_{max}$ =0.484 e · Å⁻³ and $(\Delta p)_{min}$ =-1.278 e · Å⁻³. Thermal behavior of $\{K[CH(NO_2)_2]\}_n$ was studied by DSC and TG-DTG methods. DSC result presented two exothermic processes. The self-accelerating decomposition temperature and critical temperature of thermal explosion of $\{K[CH(NO_2)_2]\}_n$ are 161.0 °C and 162.8 °C, respectively. $\{K[CH(NO_2)_2]\}_n$ presents lower thermal stability than K(DNDZ) and K(AHDNE), but higher thermal stability than K(NNMPA). $\{K[CH(NO_2)_2]\}_n$ is relatively insensitive.

Key words: 1-amino-1-hydrazino-2,2-dinitroethylene; potassium dinitromethane; crystal structure; thermal behavior

1 Introduction

1, 1-Diamino-2, 2-dinitroethylene (FOX-7) is a novel high-energy and insensitive compound [1-5], and has been considered as the main component to be used in insensitive ammunitions and solid propellants in future. Though the molecular composition and structure of FOX-7 are very simple, its chemical reactivity is surprising [6-7]. 1-Amino-1-hydrazino-2, 2-dinitroethylene (AHDNE) is a nucleophilic substitution derivative of FOX-7. AHDNE still belongs to "push-pull" nitroenamine compound[8], and has the same characteristics to FOX-7. Some energetic salts of AHDNE, such as potassium salt [K(AHDNE)] and guanidinium salt [G(AHDNE)], have been reported^[9-11]. Like many complexes of FOX-7^[12-15], some metal complexes (Cd, Zn and Ni) of AHDNE were expected to be synthesized, using K(AHDNE) as a raw material. But the result shows that potassium dinitromethane {K CH $(NO_2)_2$] $_n$ was obtained with the fracture of carbon-carbon double bond of AHDNE- anion in ammonia water at room temperature, which was caused by the addition of Zn²⁺ with the solution exhibiting strong alkalinity.

 $\{K[CH(NO_2)_2]\}\}_n$ was first synthesized by Villiers with a quite low yield in 1884, through the reduction of potassium

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bromonitromethane with hydrogen sulfide [16]. Feuer obtained this salt with a yield of 23% by Ter Meer reaction of chloronitromethane [17]. Noble reported that $\{K[CH(NO_2)_2]\}_n$ can be prepared from the alkali metal salts of dinitroethane [18]. Grakauskas improved the yield to 33% through the synthetic routine of methylcyano dinitromethane acetic acid or methyl dinitro acetic acid [19]. In recent years, some organic salts of dinitromethane, such as 1,3-dimethylimidazolium dinitromethane, ammonium dinitromethane, and 1-butyl-3-methyl-imidazolium dinitromethane, have been reported to be potential energetic materials [19-21].

In this paper, we reported crystal structure of potassium dinitromethane, investigate its thermal behavior by DSC and TG/DTG, and compared with three similar potassium salts, aiming at enriching the research studies of energetic materials.

2 Experiments

2.1 Sample

FOX-7 was obtained from Xi'an Modern Chemistry Research Institute. K(AHDNE) was prepared according to Ref. [11].

 $\{K \ [CH \ (NO_2)_2]\}_n$ was obtained by dissolving $Zn(NO_3)_2(0.357 \ g, 1.2 \ mmol)$ and $K(AHDNE) \ (0.402 \ g, 2 \ mmol)$ in ethylenediamine aqueous solution $(6 \ mL)$. In this reaction system, C = C bond was broken due to the strong alkalinity of the solution at room temperature and the catalytic influence of Zn^{2+} . Many yellow crystals of $\{K[CH(NO_2)_2]\}_n$ were formed, which were filtered, washed with distilled water and dried under vacuum, yielding $0.461 \ g \ (32\%) \ (Scheme 1)$.

FT-IR (KBr, ν / cm⁻¹): 3146, 1463, 1413, 1365, 1300, 1208, 1079, 1001, 785, 746, 690; Elemental Anal. Calcd. for CHN₂O₄K(%): C 7.28, H 0.80, N 20.10(%); Found: C 7.25, H 0.83, N 20.15 %.

Scheme 1 Synthetic route of $\{K[CH(NO_2)_2]\}_n$

2.2 Equipments and Conditions

Elemental analyses were performed on a VarioEL III elemental analyzer (Elemental Co. , Germany). IR spectra were determined on EQUINX55 with KBr pellets. DSC curves under a nitrogen atmosphere at a flow rate of 20 mL \cdot min⁻¹ were obtained by using a DSC 200 F3 media (NETZSCH, Germany), heating rates used were 5. 0, 7. 5, 10. 0 $^{\circ}$ C \cdot min⁻¹ and 12.5 $^{\circ}$ C \cdot min⁻¹ from ambient temperature to 400.0 $^{\circ}$ C, respectively. TG-DTG experiment was performed using a SDT-Q600 apparatus (TA, USA) under the condition of flow nitrogen gas at a flow rate of 100 mL \cdot min⁻¹. The heating rate used was 10. 0 $^{\circ}$ C \cdot min⁻¹ from ambient temperature to 400.0 $^{\circ}$ C. The impact sensitivity was determined by using a ZBL-B impact sensitivity instrument (NACHEN, China). The mass of drop hammer is 2.5 kg. The sample mass is 30 mg.

2.3 Determination of the Single Crystal Structure

The crystal with dimensions of 0.39 nmx0.21 nmx0.19 mm was chosen for X-ray diffraction. The data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo K_{α} radiation ($\lambda=0.071073$ nm). The structure was solved by the direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms $^{[22-23]}$. Crystal data and refinement results of $\{K[\,CH(\,NO_2\,)_2\,]\,\}_n$ are summarized in Table 1 (CCDC No. : 1059465.

3 Results and Discussion

3.1 Crystal Structure

 $\{K[CH(NO_2)_2]\}_n$ crystallizes in the triclinic system with space group *P*-1 containing two molecules per unit cell. The minimum asymmetric unit, coordinated environments of K^+ ion and crystal packing are shown in Figs. 1–3. Selected bond

lengths and bond angles are listed in Table 2.

Table 1 Crystal data and structures refinement details

chemical formula	$K[CH(NO_2)_2]$
formula mass/g · mol ⁻¹	144.14
temperature /K	296(2)
wavelength/nm	0.071073
crystal system	triclinic
space group	P-1
a/Å	4.5285(11)
b/Å	7.0377(17)
c/Å	7.8543(19)
α/(°)	70.671(3)
β/(°)	88.557(3)
γ/(°)	75.818(4)
V /Å 3	228.58 (10)
Z	2
$D_{\rm c}/{\rm g\cdot cm^{-3}}$	2.094
absorption coefficient/mm ⁻¹	1.077
F(000)	144.0
θ/(°)	2.75-25.00
index ranges	$-3 \le h \le 5$, $-6 \le k \le 8$, $-9 \le l \le 9$
reflections collected	804
reflections unique	778
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	1.060
final R indices $[I>2\sigma(I)]$	$R_1 = 0.0457$, $wR_2 = 0.1399$
R indices (all data)	$R_1 = 0.0473$, $wR_2 = 0.1364$
largest diff. peak	0.484 and -1.278
and hole/e · Å ⁻³	

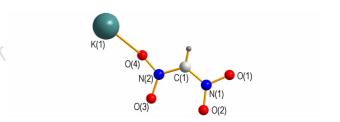


Fig. 1 Minimum asymmetric unit of $\{K[CH(NO_2)_2]\}_n$

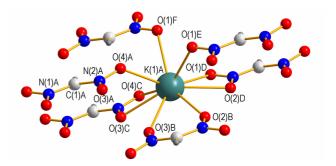


Fig. 2 Coordinated environments of K⁺ ion

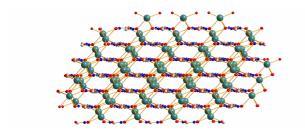


Fig. 3 Crystal packing of $\{K[CH(NO_2)_2]\}_n$

The crystallographic studies show that $\{K[CH(NO_2), 1]\}_n$ consists of a K^+ ion and a $[CH(NO_2)_2]^-$ anion (Fig. 1). Delocalization of the negative charge on the entire [CH(NO₂)₂] anion is evident from these bond lengths combined with the planarity: bond lengths of C(1)-N(2) (0.13640 nm) and C(1)—N(1) (0.13715 nm) are much shorter than the average value for a normal C—N single bond $(0.147 \text{ nm})^{[24]}$, but significantly longer than the normal C = N double bond (0.134 nm)^[24]. A similar trend is observed by corresponding N—O bonds of $[CH(NO_2)_2]^-$ anion [N(2)-O(4) (0.12596 nm),N(2)—O(3) (0. 12522 nm), N(1)—O(1) (0. 12499 nm), N(1)—O(2) (0.12411 nm), which are greatly longer than a normal N = O double bond but shorter than a N-O single bond. From the selected bond angles [N(2)-O(4)-K(1) (135.3°) , O(3)—N(2)—O(4) (120.0°) , O(3)—N(2)—C(1) $(124.4^{\circ}), O(4) - N(2) - C(1)(115.6^{\circ}), N(2) - C(1) - N(1)$

 $\begin{array}{l} (122.8^\circ)\,, O(2) - N(1) - O(1)\,(119.8^\circ)\,, O(2) - N(1) - C(1) \\ (124.3^\circ)\,, \ O(1) - N(1) - C(1)\,\,(115.9^\circ)\,]\,, \ \text{it can be seen that the} \\ \text{structure is distorted. The } - NO_2 \ \text{and } - \text{CH} \ \text{groups in the anion} \\ \text{are almost coplanar, which is supported by the torsion angles} \\ [\ O(3) - N(2) - C(1) - N(1)\,\,(6.2^\circ)\,, \ O(4) - N(2) - C(1) - N(1) \\ (-171.4^\circ)\,, \ N(2) - C(1) - N(1) - O(2)\,\,(-9.8^\circ)\,, \ N(2) - C(1) - N(1) - O(1)\,\,(169.7^\circ)\,]\,, \ \text{and the torsion angles between } \\ [\ CH(NO_2)_2\,]^- \ \text{are} \ [\ K(1) - O(4) - N(2) - O(3)\,\,(89.7^\circ)\,, \\ K(1) - O(4) - N(2) - C(1)\,\,(-92.6^\circ)\,]\,. \end{array}$

Fig. 2 indicates that each K+ ion is connected with six adjacent [CH(NO2)2] anions through eight K-O coordinated bonds [K(1)-O(2)] B#2 (0.28152] nm), K(1)-O(3) B#2 (0.28007 nm), K(1) - O(4) C + I(0.30856 nm), K(1) - O(3)C#1(0.27978 nm), K(1) - O(1)D#3 (0.30690 nm), K(1) -O(2)D#3 (0.28039 nm), K(1)-O(1)E#4 (0.28037 nm),K(1)—O(1) F#5 (0.29853 nm) ☐ and one K—O coordination bond [K(1)-O(4)A(0.28694 nm)], forming a special structure with K⁺ ion being coordination center. Atom O(4)A, O(1)E and O(1)F are three ends of this badly distorted structure, according to the selected bond lengths and bond angles (Table 2). Each [CH (NO,),] anion interacts with six adjacent K ions through the same coordination interactions simultaneously. Herein, the weak K-K interactions [K(1)-K(1)#6 (0.44623 nm)], [K(1)-N(1) #3 (0.33370 nm)] and [K(1)-N(2) #1](0.33411 nm) can also be found.

Table 2 Selected bond lengths and bond angles of $\{K[CH(NO_2)_2]\}_n$

bond	length/ nm	bond	angle/(°)	bond	angle/(°)
K(1)—O(4)A	0.28694 (30)	O(1)E#4—K(1)—O(4)A	74.33(9)	O(3)B#2-K(1)-O(2)B#2	56.56(8)
K(1)—O(2)B#2	0.28152 (30)	O(2)B#2-K(1)-O(4)A	103.15(9)	O(3)B#2-K(1)-O(1)D#3	141.99(10)
K(1)—O(3)B#2	0.28007 (31)	O(2)D#3-K(1)-O(4)A	151.45(10)	O(3)B#2-K(1)-O(4)C#1	104.42(8)
K(1) - O(4) C#1	0.30856 (32)	O(3)B#2-K(1)-O(4)A	68.63(10)	O(3)B#2-K(1)-N(1)#3	132.61(9)
K(1)—O(3)C#1	0.27978 (30)	O(3)C#1-K(1)-O(4)A	72.18(9)	O(3)B#2-K(1)-N(2)#1	84.44(8)
K(1) - O(1) D#3	0.30690 (32)	O(1)B#2-K(1)-O(4)C#1	141.07(10)	O(3)C#1-K(1)-O(3)B#2	63.60(10)
K(1) - O(2) D#3	0.28039 (30)	O(1)D#3-K(1)-O(4)C#1	67.73(8)	O(3)C#1—K(1)—O(2)D#3	136.01(11)
K(1)—O(1)E#4	0.28073 (30)	O(1)D#3-K(1)-N(1)#3	21.99(7)	O(3)C#1—K(1)—O(1)E#4	146.47(10)
K(1) - O(1) F#5	0.29853 (33)	O(1)D#3-K(1)-N(2)#1	89.36(7)	O(3)C#1-K(1)-O(2)B#2	116.13(9)
K(1)—K(1)#6	0.44623(18)	O(1)E#4-K(1)-O(2)B#2	70.28(9)	O(3)C#1—K(1)—O(1)D#3	108.30(9)
K(1) - N(1) #3	0.33370 (33)	O(1)E#4-K(1)-O(1)D#3	100.73(9)	O(3)C#1-K(1)-O(4)C#1	43.05(8)
K(1)—N(2)#1	0.33411 (28)	O(1)E#4-K(1)-N(1)#3	86.38(8)	O(3)C#1-K(1)-N(1)#3	126.07(9)
O(4)-N(2)	0.12596 (40)	O(1)E#4-K(1)-N(2)#1	151.49(8)	O(3)C#1-K(1)-N(2)#1	21.26(8)
N(2) - O(3)	0.12522 (40)	O(2)B#2-K(1)-O(1)D#3	105.11(8)	O(4)C#1-K(1)-N(1)#3	88.71(8)
N(2)-C(1)	0.13640 (47)	O(2)B#2-K(1)-N(2)#1	132.87(9)	O(4)C#1-K(1)-N(2)#1	22.15(7)
C(1)-N(1)	0.13715 (50)	O(2)B#2-K(1)-N(1)#3	84.66(8)	O(4)E#4-K(1)-O(4)C#1	147.54(9)
N(1)—O(2)	0.12411 (43)	O(2)D#3-K(1)-O(1)E#4	77.29(9)	N(2)-O(4)-K(1)	135.3(2)
N(1) - O(1)	0.12499 (41)	O(2)D#3-K(1)-O(2)B#2	63.72(10)	O(3)-N(2)-O(4)	120.0(3)
Ms.	XX	O(2)D#3-K(1)-O(1)D#3	42.75(8)	O(3)-N(2)-C(1)	124.4(3)
JSU.	KI	O(2)D#3-K(1)-O(4)C#1	106.66(9)	O(4)-N(2)-C(1)	115.6(3)
FIRE		O(2)D#3-K(1)-N(1)#3	21.11(8)	N(2)-C(1)-N(1)	122.8(3)
		O(2)D#3-K(1)-N(2)#1	125.07(9)	O(2)-N(1)-O(1)	119.8(3)
		O(3)B#2-K(1)-O(2)D#3	115.41(9)	O(2)-N(1)-C(1)	124.3(3)
		O(3)B#2—K(1)—O(1)E#4	102.42(9)	O(1)-N(1)-C(1)	115.9(3)

 $Note: \#1: x-1, \ y, \ z; \ \#2: \ -x+2, \ -y+1, \ -z+2; \ \#3: \ x-1, \ y, \ z-1; \ \#4: \ x, \ y, \ z-1; \ \#5: \ -x+1, \ -y+2, \ -z+2; \ \#6: \ -x+1, \ -y+2, \ -z+1; \ \#7: \ -x+1, \$

No hydrogen bonding is observed in the crystal packing (Fig. 3), the crystal packing is highly ordered, which means the infinite expansion of the unit involving central K^{+} and K—O bonds that connect the adjacent structures, exiting a regular configuration.

3.2 Thermal Behavior

Typical DSC and TG-DTG curves (Fig. 4 and Fig. 5) indicate that the thermal decomposition of $\{K[CH(NO_2), j]\}_n$ can be divided into two obvious exothermic decomposition stages. The first stage is a slight decomposition process, occurring at 165-195 °C with a mass loss of about 54.8%, and the extrapolated onset temperature and peak temperature at the heating rate of 10.0 $^{\circ}$ C • min⁻¹ are 172.8 $^{\circ}$ C and 178.2 $^{\circ}$ C, respectively. The second stage is an intense exothermic decomposition process with a mass loss of about 23.2 % at the temperature range of 195-240 °C, and the extrapolated onset temperature and peak temperature at the heating rate of 10.0 °C ⋅ min⁻¹ are 224.9 and 225.6 $^{\circ}$ C, respectively. The final residue at 400 $^{\circ}$ C is about 16.4%. Comparing $\{K[CH(NO_2)_2]\}_n$ with some similar potassium salts like K(NNMPA)^[25], K(AHDNE)^[10] and K(DNDZ) [26], it can be seen that their thermal behaviors are all divided into two exothermic decomposition processes. Correspondingly, the extrapolated onset temperatures and peak temperatures of the first stages are 146.7 °C and 152.3 °C for K(NNMPA), 179.8 ℃ and 181.9 ℃ for K(AHDNE), 220.4 and 222.7 °C for K(DNDZ) respectively, indicating that the thermal stability of these four potassium salts is ordered as $K(DNDZ)>K(AHDNE)>\{K[CH(NO_2),]\}_n>K(NNMPA).$

A multiple heating method was employed to obtain the kinetic parameters [the apparent activation energy(E) and pre-exponential factor (A)]. The DSC data and results obtained by Kissinger method and Ozawa method of the first exothermic decomposition process for $\{K[CH(NO_2)_2]\}_n$ are listed in Table $3^{[27-28]}$. The apparent activation energy obtained by Kissinger method agrees well with that by Ozawa method. The linear correlation coefficients (r) are very close to 1. So, the results are credible. Moreover, the apparent activation energy is lower, indicating that $\{K[CH(NO_2)_2]\}_n$ easily decomposes at high temperature.

The self-accelerating decomposition temperature ($T_{\rm SADT}$) and critical temperature of thermal explosion ($T_{\rm b}$) are two important parameters required to ensure safe storage and process operations for energetic materials and then to evaluate the thermal stability. $T_{\rm SADT}$ and $T_{\rm b}$ can be obtained by Eqs. (1) and (2) [29-30, 32], respectively.

$$T_{\text{SADT}} = T_{\text{e0}} = T_{\text{ei}} - n\beta_i - m\beta_i^2 \quad i = 1 - 4$$
 (1)

$$T_{\rm b} = \frac{E_{\rm O} - \sqrt{E_{\rm O}^2 - 4E_{\rm O}RT_{\rm e0}}}{2R} \tag{2}$$

where E_0 is the apparent activation energy obtained by Ozawa method, kJ·mol⁻¹; n and m are coefficients.

 T_{SADT} and T_{b} for $\{\text{K}[\text{CH}(\text{NO}_2)_2]\}_n$ are 161.0 °C and 162.8 °C respectively, which are lower than these of K(ANDNE) (162.5 °C and 171.4 °C) [11] and these of K(DNDZ) (196.0 °C and 208.6 °C) [26], but higher than that of K(NNMPA) as 137.4 °C and 146.3 °C [31].

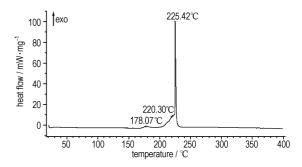


Fig. 4 DSC curve of $\{K [CH(NO_2)_2]\}_n$ at a heating rate of $10 \% \cdot min^{-1}$

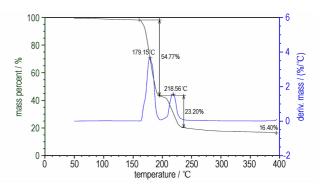


Fig. 5 TG/DTG curves of { K [CH (NO $_2$) $_2$] } $_n$ at a heating rate of 10 $^{\circ}$ C \cdot min⁻¹

Table 3 The parameters determined by DSC curves at different heating rates (β)

β /°C · min ⁻¹	T _e /℃	<i>T</i> _p / ℃	$E_{\rm K}/{\rm kJ \cdot mol^{-1}}$	$\log(A/s^{-1})$	r _K	$E_{\rm O}/{\rm kJ}\cdot{\rm mol}^{-1}$	r _O
5.0	164.8	169.4					
5.0 7.5	169.4	174.4	125.5	12.61	0.9996	126.4	0.9997
10.0	172.8	178.2	123.3		0.9996		
12.5	176.8	181.0					

Note: Subscript K, data obtained by Kissinger method; subscript O, data obtained by Ozawa method.

3.3 Sensitivity

The test result indicates that impact sensitivity of $\{K[CH(NO_2)_2]\}_n$ is >15.7 J. $\{K[CH(NO_2)_2]\}_n$ is relatively insensitive. The sensitivity is much lower than that of K(AHDNE) (> 5 J), but slightly higher than that of K(NNMPA) (>16.7 J) [31].

4 Conclusions

Potassium dinitromethane $\{K[CH(NO_2)_2]\}_n$ was synthesized and structurally characterized. $\{K[CH(NO_2)_2]\}_n$ crystallizes in triclinic system with space group P-1 containing two molecules per unit cell. The thermal behavior of $\{K[CH(NO_2)_2]\}_n$ presents two exothermic decomposition processes. The self-accelerating decomposition temperature and critical temperature of thermal explosion of $\{K[CH(NO_2)_2]\}_n$ are 161.0 °C and 162.8 °C respectively. $\{K[CH(NO_2)_2]\}_n$ exhibits lower thermal stability than K(DNDZ) and K(AHDNE), but higher thermal stability than K(NNMPA). $\{K[CH(NO_2)_2]\}_n$ is relatively insensitive.

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二硝基甲烷钾盐的晶体结构与热行为

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