

Original article

Synthesis and properties of potassium 5,5'-azobis(1-nitraminotetrazolate): A green primary explosive with superior initiation power



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ABSTRACT

Potassium 5,5'-azobis(1-nitraminotetrazolate), (K_2 ABNAT), a new green primary explosive, was synthesized via a safe and convenient synthetic procedure based on methylcarbazate and cyanogen azide. The compound was characterized by single-crystal X-ray diffraction, IR spectroscopy, Raman spectroscopy, multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). With the calculated (CBS-4M) heat of formation (617.0 kJ/mol) and the room temperature X-ray density (2.11 g/cm³), impressive values for the detonation parameters such as detonation velocity (8367 m/s) and pressure (31.5 GPa) were computed using the EXPLO5 program. The superior calculated energetic performance show it could serve as a green replacement for the widely used primary explosive, lead(II) azide, which contains toxic ingredient.

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1. Introduction

The explosive chain reaction is typically initiated by detonation of a small quantity of highly sensitive, primary explosive in a variety of military purposes and civilian applications [1]. Primary explosives form a group of explosives that, upon ignition, undergo an extremely rapid deflagration-to-detonation transition (DDT) [2–4]. These compounds are widely used in detonators, primers, blasting caps, and initiators. The primary explosives are commonly lead(II) azide, lead styphnate [5], copper(I) 5-nitrotetrazolate (DBX-1) [6], and recently reported potassium 1,1'-dinitramino-5,5'-bistetrazolate (K_2 DNABT) [7] and potassium 4,5-bis(dinitromethyl)furoxannate (K_2 BDNMF) [8] (Fig. 1). Among these compounds, lead(II) azide is the most widely used primary explosive today. However, in recent years, lead-based primary explosives have been documented to cause environmental and health related problems. Lead is both an acute and chronic toxin, and the human body has difficulty in eliminating it once it has been absorbed and dissolved in the blood [2]. As environmental regulations and

human health problems have called for the replacement of lead(II) azide in primary explosive formulations [9], a renewed focus on lead-free-alternative (copper, potassium and silver) energetics has unveiled promising properties for their use as a direct drop-in replacement of the undesirable lead and mercury-based legacy primary explosives [10]. Therefore, there is a need to develop “green” primary explosives to replace lead-based energetic compounds. A “green” replacement of lead-based compounds should possess the following properties: (a) insensitivity to light; (b) sensitivity to detonation (but not too sensitive to handle and transport); (c) stability to at least 150 °C; (d) stability upon storage for long periods of time; (e) free of toxic metals or other known toxins; (f) possess high detonation performance and (g) an ease, safety, and affordability of synthesis [2,5].

In seeking “green” replacements for the lead-based compound, one important strategy we focused on is the use of nitrogen-rich energetic compounds. These are widely considered to be viable environmental energetics as the main detonation product is nitrogen gas. At the same time, they always possess high positive heats of formation, which lead to high energy output [2]. As is well-known, potassium is an environmentally friendly species with good coordinating ability to energetic ligands [11]. Therefore, nitrogen-rich, energetic potassium salts are considered to be

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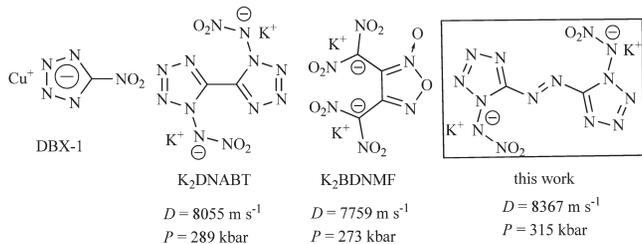


Fig. 1. Promising replacements of lead-based primary explosives.

“green” candidates for the replacement of lead-based primary explosives. In our present work, we focus our attention on the “green” primary explosives with high detonation performance. As a result of our continuing efforts, we report, herein, the synthesis of a new green primary explosive, potassium 5,5'-azobis(1-nitraminotetrazolate) (K₂ABNAT), which contains only potassium as the metal (Scheme 1).

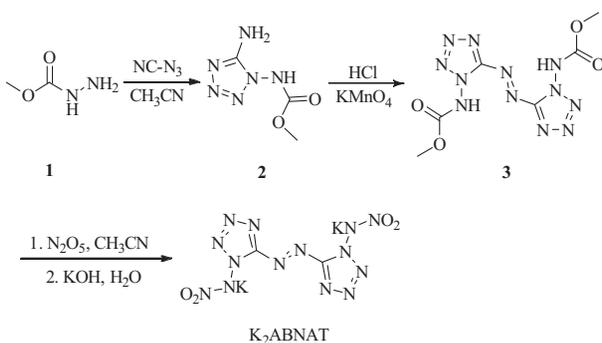
2. Experimental

All chemical reagents and solvents were used as supplied unless otherwise stated. Elemental analyses (C, H and N) were performed on a VARI-EL-3 elementary analysis instrument. Infrared spectra were obtained as KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000–400 cm⁻¹. Raman spectra were measured with a RENISHAW[®] InVia instrument. The ¹H NMR and ¹³C NMR data were obtained in DMSO-*d*₆ on a Bruker AV500 NMR spectrometer. The DSC experiment was performed using a DSC-Q200 apparatus (TA Instruments, New Castle, USA) under a nitrogen atmosphere at a flow rate of 50 mL/min with about 0.3 mg of the sample sealed in aluminium pans for the DSC measurements. The TG/DTG experiment was performed using a SDT-Q600 apparatus (TA Instruments, New Castle, USA) under a nitrogen atmosphere at a flow rate of 50 mL/min.

2.1. Preparation of 1-methoxycarbonyl-1,5-diaminotetrazole (2)

Methylcarbazate (1) (1.65 g, 18.1 mmol) in water (10 mL) was added to a freshly prepared solution of cyanogen azide in acetonitrile (22.3 mmol in 40 mL) at ice water condition, and stirring at r.t. for 24 h. After most of the acetonitrile evaporation, the solution was stirred until a white filterable suspension was formed. The suspension was filtered and washed with a small quantity of ice water. The product was dried in air.

Compound 2: White solid (1.58 g, 54.5%); mp: 180.5 °C, T_{dec} : 185.5 °C (peak, 5 °C/min); IR (KBr, cm⁻¹): 3373, 3263, 3200, 3104, 2867, 1743, 1655, 1580, 1485, 1451, 1326, 1198, 1119, 1069, 987, 926, 829, 758, 723; Raman (785 nm, 250 mW, cm⁻¹): 2969, 2873,



Scheme 1. Synthetic pathway of K₂ABNAT.

1749, 1657, 1582, 1512, 1487, 1453, 1342, 1120, 1073, 989, 927, 831, 773, 758, 666 521, 450, 373; ¹H NMR (500 MHz, DMSO-*d*₆): δ 11.21 (s, 1H, NH), 7.05 (s, 2H, NH₂), 3.73 (s, 3H, CH₃); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 155.14, 155.05, 53.59; Elemental analysis: calcd. (%) for C₃H₆N₆O₂ (158.06): C 22.79, H 3.82, N 53.15, found: C 22.86, H 3.76, N 53.34.

2.2. Preparation of 5,5'-azobis(1-methoxyformamidotetrazole) (3)

Compound 2 (0.79 g, 5 mmol) was added to concentrated hydrochloric acid (12.9 mL) at r.t. with stirring until the solid was dissolved. Potassium permanganate (0.79 g, 5 mmol) in water (14 mL) was added dropwise to the stirred solution of 2 at 10 °C. After stirring for 10 min, the reaction mixture was heated to 55 °C for 5 h. The yellow precipitate was filtered, washed with ice water and dried in air.

Compound 3: Yellow solid (0.70 g, 89.7%); T_{dec} : 190.9 °C (peak, 5 °C/min); IR (KBr, cm⁻¹): 3242, 3024, 2968, 1767, 1638, 1536, 1504, 1467, 1437, 1309, 1248, 1147, 1074, 1049, 964, 848, 767, 751, 594; Raman (785 nm, 250 mW, cm⁻¹): 2974, 1780, 1508, 1443, 1433, 1247, 1084, 1046, 983, 932, 813, 524, 403; ¹H NMR (500 MHz, DMSO-*d*₆): δ 12.84 (s, 2H, 2NH), 3.81 (s, 6H, 2CH₃); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 158.00, 155.24, 54.47; Elemental analysis: calcd. (%) for C₆H₈N₁₂O₄ (312.08): C 23.08, H 2.58, N 53.84; found: C 23.13, H 2.52, N 53.90.

2.3. Preparation of potassium 5,5'-azobis(1-nitraminotetrazolate) (K₂ABNAT)

Compound 3 (1.87 g, 6 mmol) was suspended in dry acetonitrile (58 mL) and cooled to 0 °C, then N₂O₅ (2.59 g, 24 mmol) in dry acetonitrile (32 mL) was added in one portion and the mixture stirred at 0 °C for 4 h. The reaction was quenched by adding KOH (2.69 g, 48 mmol) dissolved in water (24 mL), and stirred vigorously for another one hour. The solvent was removed under high vacuum. The residue was stirred in methanol (35 mL) for several hours. The precipitated solid was filtered and suspended in 20 mL of ice water, stirred for 20 min, filtered again and dried in air.

Compound K₂ABNAT: Yellow solid (0.46 g, 21.2%); T_{dec} : 194.3 °C (peak, 5 °C/min); IR (KBr, cm⁻¹): 1635, 1456, 1431, 1298, 1242, 1226, 1154, 1079, 1015, 927, 775; Raman (785 nm, 250 mW, cm⁻¹): 1491, 1480, 1432, 1400, 1313, 1245, 1227, 1090, 1081, 1017, 997, 927, 879, 822, 684, 430, 372, 291; ¹³C NMR (125 MHz, DMSO-*d*₆): δ 157.96; Elemental analysis: calcd. (%) for C₂K₂N₁₄O₄ (361.95): C 6.63, N 54.12; found: C 6.71, N 54.06.

3. Results and discussion

K₂ABNAT was obtained in three steps from methylcarbazate (1) and cyanogen azide, and the synthetic process was described as follows. Compound 1 was reacted with cyanogen azide to yield *N*-methoxycarbonyl protected 1,5-diaminotetrazole (2), which was oxidized in concentrated hydrochloric acid with KMnO₄ to 5,5'-azobis(1-ethoxyformamidotetrazole) (3). Compound 3 was gently nitrated with N₂O₅ in acetonitrile, and decomposed in solution with aqueous KOH to give the mixture of K₂ABNAT and KNO₃ as a yellow precipitate, from which K₂ABNAT is isolated by stirring in water and methanol, respectively. K₂ABNAT is insensitive to light and very stable upon storage under ambient conditions. It is not soluble in methanol or ethanol, but could dissolve in *N,N'*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).

Single crystals of K₂ABNAT suitable for X-ray diffraction measurements were obtained by slow-evaporation from a water solution. The molecular structure of K₂ABNAT in the solid state was determined by X-ray diffraction at r.t. to obtain accurate density for performance calculations. The ORTEP diagram of K₂ABNAT is

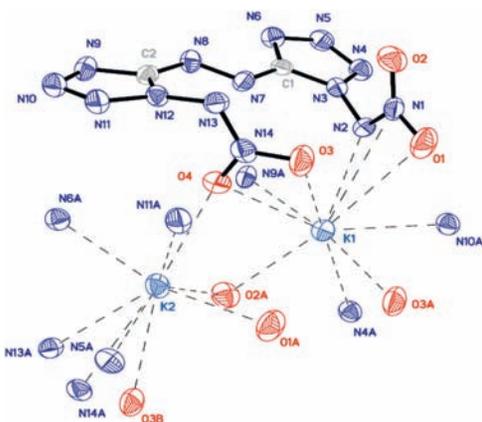


Fig. 2. Single crystal structure of K_2ABNAT . Thermal ellipsoids represent the 50% probability level.

shown in Fig. 2, and more structural details are given in the Supporting information. The compound crystallizes in the triclinic space group $P\bar{1}$ with a density of 2.11 g/cm^3 and a cell volume of 570.7 \AA^3 at 296 K. The repeating unit of K_2ABNAT contains two potassium ions and one 5,5'-azobis(1-nitramino tetrazolate) (ABNAT) anion. There are two different coordination environment of potassium atoms. The potassium atoms are coordinated irregularly by either the nitrogen atoms N1, N2, N4, N5, N6, N9, N10, N11, N13, N14, or the nitro oxygen atoms O1, O2, O3 and O4. Both tetrazole rings and the azo bond are almost planar to each other. The nitro groups are twisted out of this plane by almost 85° and 87° , respectively. For the K_2ABNAT molecule, the bond distances for N1–N2 (1.332(6) Å), N2–N3 (1.387(5) Å), N7–N8 (1.263(5) Å), N12–N13 (1.388(5) Å) and N13–N14 (1.323(6) Å) lie between an N–N single bond (1.460 Å) and double bond (1.250 Å) [12,13]. In addition, the bond distances of C1–N7 (1.397(6) Å) and C2–N8 (1.389(6) Å) are shorter than a C–N single bond (1.470 Å) and longer than C=N double bond (1.220 Å) [12], which can be explained by the hyper conjugation effect of good delocalization of π electron in the whole molecule structure (data and parameters of the X-ray measurements and structure refinements are given in Table S1 in Supporting information. File CCDC-1439593 contains supplementary crystallographic data of K_2ABNAT which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif).

The thermal stability of K_2ABNAT was also investigated using differential scanning calorimetry (DSC) and thermogravimetric (TG/DTG). In the DSC curve (Fig. 3), decomposition started at 189.4°C (onset temperature) and a peak temperature of 194.2°C when the heating rate is 5°C/min . There is no endothermic peak in the DSC curve which indicates K_2ABNAT melts with concomitant

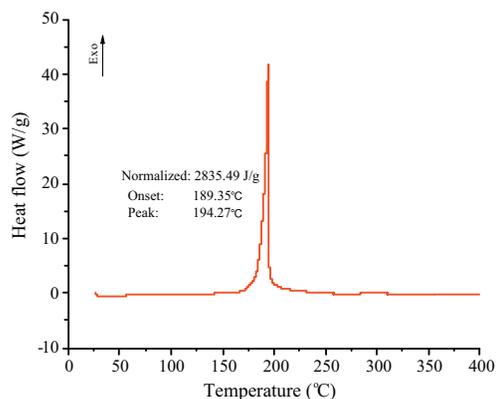


Fig. 3. DSC curve of K_2ABNAT at heating rate of 5°C/min .

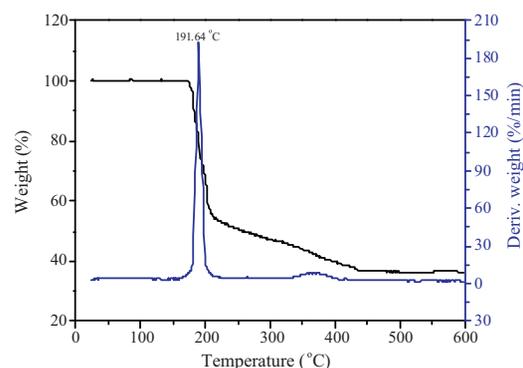


Fig. 4. TG/DTG curves of K_2ABNAT at heating rate of 5°C/min .

decomposition under the heating condition. The typical TG/DTG curves of K_2ABNAT are shown in Fig. 4. As noticeable from the TG curve, there was one main mass-loss stage, corresponding to only one peak in the DSC curve (Fig. 3). A sudden weight loss was observed at 175.0°C that stopped at 200.0°C , and the mass-loss peak was at 191.6°C .

The impact sensitivity test was carried out according to the Fall Hammer Method using a 2.0 kg drop hammer on a ZBL-B impact sensitivity instrument. The friction sensitivity test was determined using a Julius Peters apparatus, following the BAM method [14]. Compound K_2ABNAT is very sensitive towards impact (1–2 J) and friction ($\leq 1 \text{ N}$), these properties are comparable to those of lead(II) azide and K_2DNABT . Therefore, it should be considered to be a primary explosive with handling by appropriate precautions.

In order to explore the energetic performance of K_2ABNAT , several detonation parameters were calculated with the EXPLO5

Table 1
Comparison of physicochemical and energetic properties of lead(II) azide, K_2DNABT and K_2ABNAT .

Compound	$Pb(N_3)_2$ [11]	K_2DNABT [11]	K_2ABNAT
Formula	N_6Pb	$C_2K_2N_{12}O_4$	$C_2K_2N_{14}O_4$
M (g/mol)	291.3	334.3	362.0
IS (J) ^a	2.5–4	1	1–2
FS (N) ^b	0.1–1	≤ 1	≤ 1
N (%) ^c	28.9	50.3	54.1
$N + O$ (%) ^d	28.9	69.4	71.8
Ω (CO) (%) ^e	–11.0	4.8	4.4
Ω (CO ₂) (%) ^f	–11.0	–4.8	–4.4
T_{dec} ($^\circ\text{C}$) ^g	315	200	189
ρ (g/cm ³) ^h	4.8	2.11	2.11
$\Delta_f H_m^\circ$ (kJ/mol) ⁱ	450.1	326.4	617.0
$\Delta_f U^\circ$ (kJ/kg) ^j	1574.9	1036.1	1764.5
$-\Delta_{ex} U^\theta$ (kJ/kg) ^k	1569	4959	5358
T_{det} (K) ^l	3401	3424	3671.1
P_{CJ} (GPa) ^m	33.4	28.9	31.5
D_{det} (m/s) ⁿ	5877	8055	8367
V_0 (L/kg) ^o	252	489	752
VST (mL/g) ^p	–	–	0.49

^a Impact sensitivity to BAM drop hammer (1 of 6).

^b Friction sensitivity to BAM drop hammer (1 of 6).

^c Nitrogen content.

^d Nitrogen and oxygen content.

^e Oxygen balance assuming the formation of CO.

^f Oxygen balance assuming the formation of CO₂.

^g Decomposition temperature (onset temperature at a heating rate of 5°C/min).

^h Crystal density at 296 K.

ⁱ Heat of formation.

^j Energy of formation.

^k Heat of detonation.

^l Temperature of detonation.

^m Detonation pressure.

ⁿ Detonation velocity.

^o Gas volume after detonation.

^p Vacuum stability test.

code [15] in its version 5.05 using density (recalculated from the X-ray structure at r.t.) and a calculated heat of formation, and compared to those of lead(II) azide and K₂DNABT. The crystal density of K₂ABNAT calculated at 296 K is 2.11 g/cm³, which is equal in value to K₂DNABT. The heat of formation of K₂ABNAT was calculated by the atomization method using the Gaussian 09 program package at the CBS-4M level of theory [16,17]. As can be seen in Table 1, the heat of formation (617.0 kJ/mol) of K₂ABNAT is much higher than lead(II) azide (450.1 kJ/mol) and K₂DNABT (326.4 kJ/mol). Based on good oxygen balance and nitrogen content, K₂ABNAT easily outperforms lead(II) azide and K₂DNABT in all critical detonation parameters (energy of formation, heat of detonation, temperature of detonation, detonation velocity, and gas volume after detonation). Therefore, K₂ABNAT displays excellent overall performance as a suitable and non-toxic replacement for lead(II) azide, with a safe and convenient synthesis in three steps from commonly available chemicals (Scheme 1), which is comparable with that of K₂DNABT.

4. Conclusion

In summary, potassium 5,5'-azobis(1-nitramino tetrazolate) (K₂ABNAT), a new green primary explosive, was synthesized in three steps from methylcarbazate and fully characterized. K₂ABNAT displays high density (2.11 g/cm³), excellent thermal stability (onset temperature 189.4 °C), high positive heat of formation (617.0 kJ/mol), remarkable energetic performances ($D = 8367$ m/s, $P = 31.5$ GPa), which easily outperforms lead(II) azide. Therefore, K₂ABNAT is predicted to be a superior energetic performance and green primary explosive, which is potential green replacement for the widely used primary explosive, lead(II) azide.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ccl.2016.06.026>.

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