Energetic Materials

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Potassium 4,5-Bis(dinitromethyl)furoxanate: A Green Primary Explosive with a Positive Oxygen Balance

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In memory of Malcolm MacKenzie Renfrew

Abstract: *Potassium 4,5-bis(dinitromethyl)furoxanate was synthesized readily from cyanoacetic acid. It was characterized by IR spectroscopy, elemental analysis, NMR spectroscopy, and differential scanning calorimetry (DSC), and the structure was confirmed by X-ray single-crystal diffraction. Its positive oxygen balance, high density (2.130 g cm^{-3}), sensitivity (IS = 2 J, FS = 5 N), and calculated heat of formation (−421.0 kJ mol^{-1}), combined with its calculated superior detonation performance (D = 7759.0 m s^{-1}, P = 27.3 GPa), make it a competitive replacement as a green primary explosive.*

Primary explosives as a class of energetic compounds show high sensitivity toward impact, friction, shock, heat, and electrostatic discharge. They are able to transition from combustion (or deflagration) to detonation (fast deflagration to detonation transition, DDT) and therefore are useful as initiators.[1] Lead-based primary explosives, such as lead azide and lead styphnate, are still the most commonly used materials in civilian and military operations. The toxicity associated with these widely used lead-based primary explosives is a source of serious environmental and health-related problems. Therefore, the development of lead-free, environmentally friendly alternatives to current primary explosives is a major current focus.[2]

Potassium is an environmentally friendly species with good coordinating ability to energetic ligands.[3] Energetic potassium salts are considered to be "green" candidates for the replacement of lead-based primary explosives. To date, several promising replacements for lead-based primary explosives have been synthesized (Figure 1).[3,4] Energetic materials with a zero or positive oxygen balance (OB) convert all carbon into carbon dioxide and all hydrogen into water. The liberation of minimum amounts of toxic gases is desirable, so they can be seen as "greener" than compounds with a negative OB. However, most reported candidates as green primary explosives have a negative OB (Figure 1).

The introduction of nitro groups is an efficient way to improve the OB of compounds. Molecules that contain dinitromethyl groups show enhanced oxygen balance and density, which in turn improve their detonation performance (pressure and velocity). Furthermore, the planarity of the dinitromethyl group makes those molecules more stable than trinitromethyl-containing molecules, which have a non-coplanar geometric structure. Dinitromethyl-containing azole-based energetic compounds have been studied extensively in the past few years.[5] A general strategy for the synthesis of dinitromethyl azoles involves the nitration of *C*-azolylacetic acid esters with a mixture of concentrated sulfuric acid and 100 % nitric acid. This transformation is followed by decarboxylation with a base and subsequent acidification. However, this method has the disadvantage of a rather small number of known *C*-azolylacetic acid esters. An alternative method is the nitration of the more accessible chloroximes by N_2O_5, followed by treatment with potassium iodide and an acid.[3,5g] Furoxan as a "hidden" nitro group possesses the highest oxygen content (37.2 %) among the N-heterocyclic rings. The combination of the dinitromethyl group with a furoxan ring dramatically improves the oxygen balance. In our continuing efforts in seek of high-energy-density materials (HEDMs), we have now synthesized and characterized a new primary explosive, potassium 4,5-bis(dinitromethyl)-furoxanate, which exhibits a positive oxygen balance and properties competitive with those of lead azide.

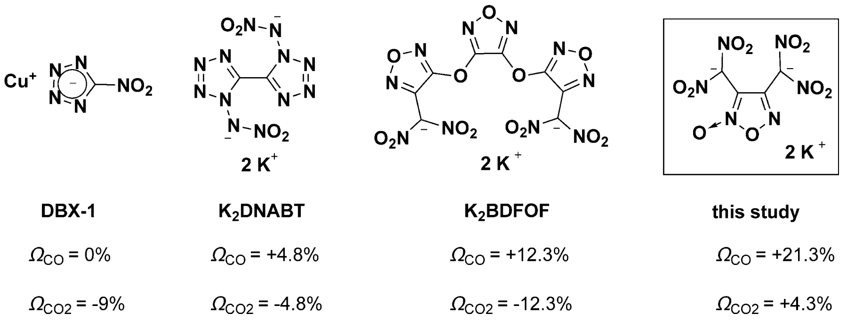

Figure 1. Green candidates for the replacement of lead-based primary explosives.

Potassium 4,5-bis(dinitromethyl)furoxanate (**5**) was obtained in five steps from cyanoacetic acid (Scheme 1). Compounds **1**–**3** were prepared according to the previously described methods.[6] The nitration of **3** was realized with a mixture of trifluoroacetic acid anhydride (TFAA) and

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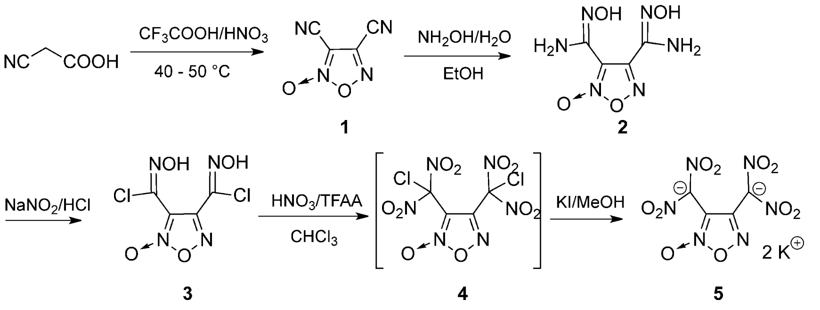

Scheme 1. Synthesis of **5**.

100% HNO_3. The reaction process was monitored by TLC (ethyl acetate/hexane 1:9). Compound **4** is a colorless oil which slowly decomposes upon standing. Therefore, **4** was treated immediately with KI in methanol, which led to the precipitation of the light-yellow solid **5**. Compound **5** was insensitive to light and very stable upon storage under ambient conditions. It was not soluble in methanol or ethanol, but did dissolve in water, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF). It started to decompose at 218 °C without melting.

The structure of **5** was confirmed by IR and ^{13}C NMR spectroscopy, elemental analysis, ^{15}N NMR spectroscopy, and X-ray diffraction. Four nitrogen signals were observed in the ^{15}N NMR spectrum. They were assigned based on GIAO NMR calculation with Gaussian 03 (Figure 2).[7] Crystals of **5** were grown in water as yellow prisms, and the single-crystal X-ray structure of **5** was determined at 100 K (Figure 3).

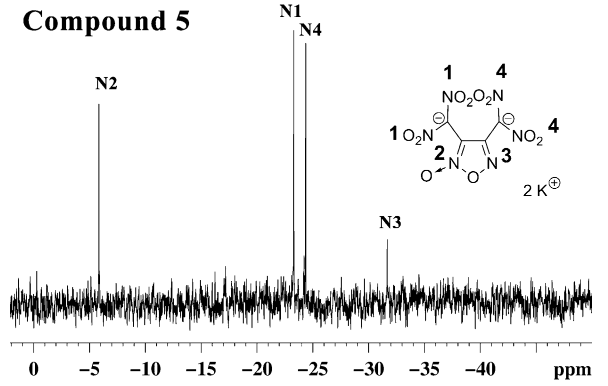

Figure 2. ^{15}N NMR spectrum of compound **5**.

Compound **5** crystallizes in the monoclinic space group $P2_1/c$, with four molecules per unit cell (Table 1). The carbon atoms C3, C4 and all the atoms in the furoxan ring are coplanar, with two of the four nitro groups located on each side of the furoxan plane. The two dinitromethane moieties are almost planar, with O7 and O4 showing the biggest deviation of 0.1897 and 0.2811 Å from the [N5, C4, N6] plane and the [N3, C3, N4] plane, respectively. Those two planes form dihedral angles of 57.193 and 55.076° with the furoxan plane. (More details about the crystal structure can be found in the Supporting Information.)

The physical properties of **5** are summarized in Table 2. It possesses a positive oxygen balance, a measured density of 2.130 $g\,cm^{-3}$ at room temperature, an impact sensitivity (IS) of 2 J, and a friction sensitivity (FS) of 5 N. These properties are comparable to those of lead azide. The heat of formation of **5** was calculated to be $-421.0\ kJ\,mol^{-1}$ by the use of the Gaussian 03 (Revision D.01) suite of programs at the level of theory of MP2/6-311++G**//B3LYP/6-31+G** through Born–Haber energy cycles (see Tables S4 and S5 in the Supporting Information).[7–9] The detonation properties were calculated by using EXPLO5 (version 6.01) code.[10] The superior detonation properties of **5** ($D = 7759.0\ m\,s^{-1}$, $P = 27.3$ GPa) as compared to those of lead azide, and the small amount of toxic materials (CO% + NO% = 0.29%) in the detonation products, make it promising as a green primary explosive (Figure 4; see Table S6 for the composition of the major detonation products).

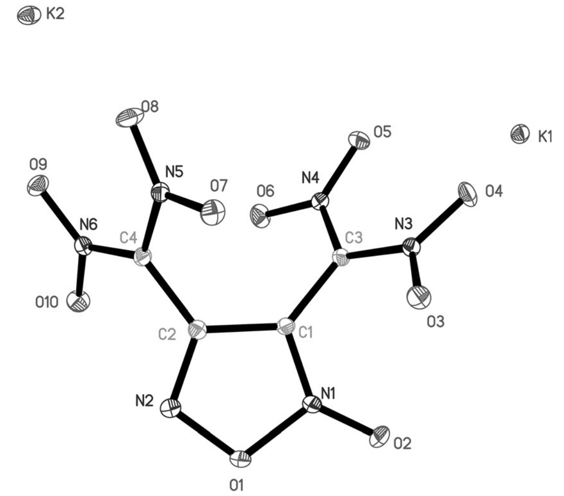

Figure 3. Crystal structure of **5** (ellipsoids are set at 50% probability).

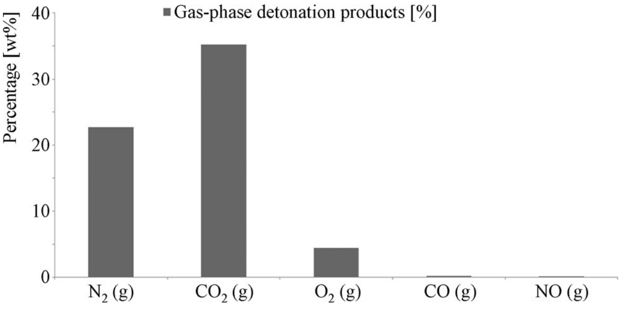

Figure 4. Composition of gas-phase detonation products for **5** [wt%].

In summary, potassium 4,5-bis(dinitromethyl)furoxanate was obtained in five steps from commercially available cyanoacetic acid through the use of a more accessible nitration method with a mixture of trifluoroacetic acid

Table 1: Crystal data and structure refinement for **5**.

Empirical formula	$C_4K_2N_6O_{10}$
Formula weight	370.30
Temperature [K]	100
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	12.3388(4)
b [Å]	7.3181(2)
c [Å]	12.6248(4)
α [°]	90
β [°]	96.2370(10)
γ [°]	90
Volume [Å^3]	1133.23(6)
Z	4
ρ_{calcd} [g cm^{-3}]	2.170
μ [mm^{-1}]	0.914
F(000)	736.0
Crystal size [mm^3]	0.2×0.15×0.15
Radiation	MoK$_\alpha$ (λ = 0.71073)
2θ range for data collection [°]	6.444–61.144
Index ranges	$-17 \leq h \leq 17$, $-10 \leq k \leq 10$, $-18 \leq l \leq 18$
Reflections collected	41 608
Independent reflections	3483 [R_{int} = 0.0357, R_{sigma} = 0.0165]
Data/restraints/parameters	3483/0/199
Goodness-of-fit on F^2	1.065
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0237, wR_2 = 0.0556
Final R indexes (all data)	R_1 = 0.0301, wR_2 = 0.0583
Largest diff. peak/hole [e Å^{-3}]	0.51/−0.22
CCDC number	1428290

Table 2: Physical properties of lead azide and compound **5**.

	$Pb(N_3)_2$	**5**
Formula	N_6Pb	$C_4K_2N_6O_{10}$
M [g mol^{-1}]	291.3	370.3
T_{dec} [°C][a]	315.0	218.3
Ω_{CO} [%][b]	−11.0	21.3
Ω_{CO_2} [%][c]	−11.0	4.3
N [%][d]	28.9	22.7
N + O [%][e]	28.9	65.9
ρ [g cm^{-3}][f]	4.800	2.130
IS [J][g]	2.5–4.0	2
FS [N][h]	0.1–1	5
ΔH_f [kJ mol^{-1}][i]	450.1	−421.0
T_{det} [K][j]	3353	3574
D [m s^{-1}][k]	5876.8	7759.0
P [GPa][l]	33.4	27.3

[a] Decomposition temperature (onset temperature at a heating rate of 5 °C min^{-1}). [b] Oxygen balance for $C_aH_bO_cN_d$: 1600 ($c-a-b/2$)/MW. [c] Oxygen balance for $C_aH_bO_cN_d$: 1600 (c−2a−b/2)/MW. [d] Nitrogen content. [e] Nitrogen and oxygen content. [f] Density, measured with a gas pycnometer (25 °C). [g] Impact sensitivity. [h] Friction sensitivity. [i] Heat of formation. [j] Detonation temperature calculated with EXPLO5 V6.01. [k] Detonation velocity calculated with EXPLO5 V6.01. [l] Detonation pressure calculated with EXPLO5 V6.01. MW = molecular weight.

anhydride and 100 % HNO_3. It has a density of 2.130 g cm^{-3}, a positive oxygen balance, and an onset (violent) decomposition temperature of 218.3 °C. The high sensitivity and remarkable detonation performance of this compound as well as the green detonation products make it a competitive candidate as a green primary explosive.

Experimental Section

Caution: All furoxan compounds are potential energetic materials and may explode under certain conditions. Appropriate safety precautions should be taken when preparing and handling.

The detailed experimental description of the entire synthetic procedure is shown in Scheme 1; compounds **1**–**3** were prepared according to previously reported methods.[6]

Compound **3** (2.41 g, 10 mmol) in $CHCl_3$ (20 mL) was added dropwise to a stirred mixture of trifluoroacetic acid anhydride (14 mL) and 100 % HNO_3 (8 mL), while maintaining the reaction temperature between −5 and 0 °C. After the addition was complete, the ice bath was removed, and the mixture was allowed to warm slowly to room temperature. It was stirred for another 2 h, and then poured into ice water (50 mL) and extracted with $CHCl_3$ (3×20 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and then concentrated under vacuum to provide the intermediate **4** as a colorless oil. Compound **4** was dissolved in methanol (20 mL), potassium iodide (4 g, 24 mmol) in methanol (30 mL) was added dropwise, and the mixture was stirred overnight at room temperature. The precipitate formed was collected by filtration and washed with cold water (5 mL) and then methanol (5 mL) and ethyl ether (10 mL) to give **5** (1.12 g, 30.2 %) as a light-yellow solid. T_{dec} (5 °C min^{-1}): 218.3 °C; IR (KBr): 1616, 1533, 1511, 1485, 1464, 1398, 1282, 1233, 1190, 1151, 1138, 991, 964, 830, 779, 749 cm^{-1}; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): 112.05, 120.60, 123.23, 152.09 ppm; $^{15}N\{^1H\}$ NMR ([D$_6$]DMSO): −5.84, −23.30, −24.35, −31.66 ppm; elemental analysis ($C_4K_2N_6O_{10}$, 370.27): calcd: C 12.97, N 22.70; found: C 13.11, N: 22.20.

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