Energetic Materials

International Edition: DOI: 10.1002/anie.201601432
German Edition: DOI: 10.1002/ange.201601432

Potassium 4,4′-Bis(dinitromethyl)-3,3′-azofurazanate: A Highly Energetic 3D Metal–Organic Framework as a Promising Primary Explosive

*Yongxing Tang, Chunlin He, Lauren A. Mitchell, Damon A. Parrish, and Jean'ne M. Shreeve**

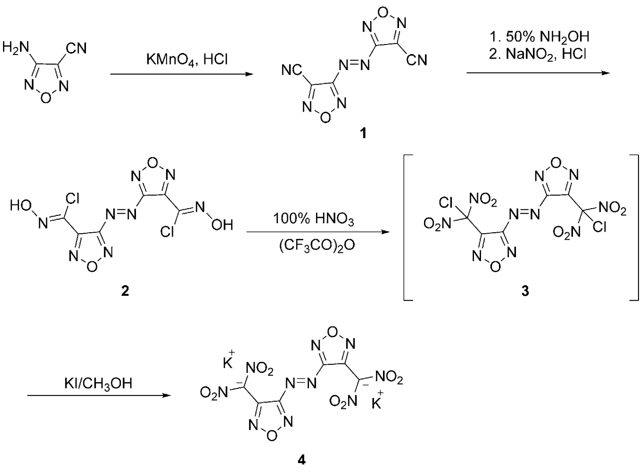
Abstract: *Environmentally acceptable alternatives to toxic lead-based primary explosives are becoming increasingly important for energetic materials. In this study, potassium 4,4′-bis(dinitromethyl)-3,3′-azofurazanate, comprising two dinitromethyl groups and an azofurazan moiety, was synthesized and isolated as a new energetic 3D metal–organic framework (MOF). Several attractive properties, including a density of 2.039 g cm^{-3}, a decomposition temperature of 229 °C, a detonation velocity of 8138 m s^{-1}, a detonation pressure of 30.1 GPa, an impact sensitivity of 2 J, and friction sensitivity of 20 N make **4** a good candidate as a green primary explosive.*

The design and synthesis of green primary explosives beyond the current lead-based systems (lead azide and lead styphnate) are important goals in the field of energetic materials.[1] There have been numerous attempts to synthesize suitable alternative candidates. Although metal-free primary explosives, including cyanuric triazide (CTA) and 2-diazo-4,6-dinitrophenol (DDNP), have been reported,[2] they do not meet the requirement of good thermal stability (>180 °C). Metal–organic primary explosives, such as copper(I) 5-nitrotetrazolate (DBX-1),[3] potassium 1,1′-dinitramino-5,5′-bis(tetrazolate) (K_2DNABT),[4] potassium 1,5-(dinitramino)-tetrazolate,[5] potassium 4,5-bis(dinitromethyl)furoxanate,[6] and other nontoxic metal–organic energetic compounds, have received considerable attention.[7] Among them, potassium salts are frequently considered as a green alternative to lead as a result of the good coordinating ability and environmentally friendly nature of this metal.

Energetic 3D metal–organic frameworks, usually based on metal-ion-containing, nitrogen-rich heterocyclic compounds, have been suggested as suitable materials for the synthesis of next-generation promising primary explosives.[8] Nitrogen-rich heterocyclic compounds as ligands play important roles in ensuring high density, high heat of detonation, and good thermal stability.[9] In particular, furazan has two C=N and two N−O bonds, which can enhance the density and oxygen balance. Subsequent introduction of an azo bridge to form the azofurazan moiety increases the heat of formation. However, in the design of primary explosives, in addition to stability, sensitivity to detonation is also an important factor. An intelligent choice is to gather energetic groups (such as NO_2, $NHNO_2$, or N_3) in a relatively small molecule. The dinitromethyl moiety should be a suitable candidate as a superior energetic functional group with good thermal stability,[6,10] unlike trinitromethyl-containing compounds that invariably have low decomposition temperatures.[11] Since the combination of the azofurazan moiety and the dinitromethyl group appears promising, the potassium salt should be a likely primary explosive candidate. With this strategy in mind, we describe herein the synthesis and characterization of potassium 4,4′-bis(dinitromethyl)-3,3′-azofurazanate (**4**).

As shown in Scheme 1, 4,4′-dicyano-3,3′-azofurazan (**1**) was prepared by the oxidation of 3-amino-4-cyanofurazan[12] according to a reported procedure.[13] Compound **1** was then treated with 50 % aqueous hydroxylamine in ethanol, followed by diazotization in dilute HCl, to form 4,4′-bis-chlorohydroximoyl-3,3′-azofurazan (**2**). The nitration of **2** with a mixture of 100 % nitric acid and trifluoroacetic acid anhydride $(CF_3CO)_2O$ resulted in the formation of intermediate **3**. Species **3** was subsequently dissolved in methanol and treated with KI to give the product potassium 4,4′-bis(dinitromethyl)-3,3′-azofurazanate (**4**).

The molecular composition of **4** was determined by ^{13}C NMR spectroscopy and elemental analysis as well as by single-crystal X-ray diffraction.[14] Compound **4** crystallizes in



Scheme 1. Synthetic route to potassium 4,4′-bis(dinitromethyl)-3,3′-azofurazanate (**4**).

---

[*] Dr. Y. Tang, Dr. C. He, Prof. Dr. J. M. Shreeve
Department of Chemistry
University of Idaho
Moscow, ID 83844-2343 (USA)
E-mail: jshreeve@uidaho.edu

Dr. L. A. Mitchell, Dr. D. A. Parrish
Naval Research Laboratory
4555 Overlook Avenue, Washington, DC 20375 (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201601432.

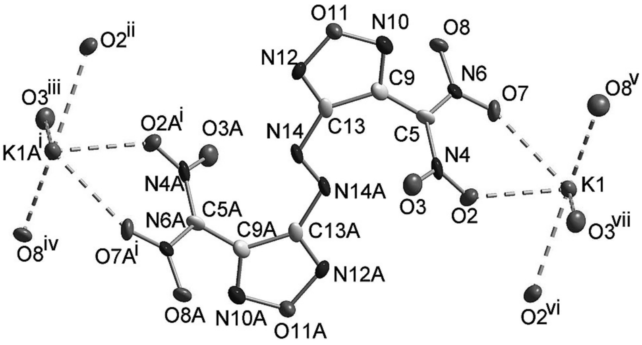


Figure 1. X-ray crystal structure of **4** with cation coordination.[14] Thermal displacement ellipsoids are set at 50% probability. Symmetry codes: i) 1−*x*, 2−*y*, −*z*; ii) 1+*x*, *y*, −1+*z*; iii) *x*, *y*, −1+*z*; iv) *x*, 1+*y*, −1+*z*; v) 1−*x*, 1−*y*, 1−*z*; vi) −*x*, 2−*y*, 1−*z*; vii) 1−*x*, 2−*y*, 1−*z*.

the triclinic space group $P\bar{1}$ with a calculated density of 2.059 g cm^{-3} at 20 °C. The molecular structure is shown in Figure 1. The azofurazan moiety together with C5 and C5A atoms are approximately in the plane, which can be seen from the C5-C9-N10-O11 torsion angle of 176.7(8)° and the N12-C13-N14-N14A torsion angle of 178.2(10)°. The dihedral angle between the two planes defined by the two nitro groups ([O7, N6, O8] and [O2, N4, O3]) is 11.245°. In addition, the plane of [N6, C5, N4] forms a dihedral angle of 53.27° with the azofurazan plane. The K ions are chelated by five oxygen atoms from nitro groups with O−K$^+$ distances ranging from 2.733(7) Å to 2.836(8) Å. Bridging nitro groups connect the K centers into chains of K-O-N-O-K that extend parallel to the *a* axis with K⋯K = 4.9299(42) Å, whereas along the *b*-axis, the K ions are bridged (K⋯K = 7.5171(34) Å) by dinitromethyl groups (Figure 2a). These chains are further linked by the azofurazan moieties to form a three-dimensional network, which indicates that **4** is a 3D MOF (Figure 2b). However, the irregular pores (A and B) in **4** are not as big as those in the other MOFs.[7,9] In **4**, the coordinate of pore A is (0.458, 0.432, 0.042) with the volume of 6.1 Å^3 judged by using a probe radius of 0.4 Å, which can be ignored due to its small volume, whereas the pores of B are much smaller (see Figure S1 in the Supporting Information). Better insight into the complicated 3D network can be attained by topology analysis (Figure 2c). In this network, each potassium(I) ion can be simplified to a 5-connected node, while each azofurazan ligand can be regarded as a 10-connected node. Therefore, the overall 3D network can be simplified as a (5,10)-connected fit network with the point symbol of $\{4^{10}\}_2\{4^{28}.6^{16}.8\}$.

To evaluate the possibility of **4** as a suitable green primary explosive candidate, the thermal stability, sensitivity towards impact and friction, as well as the detonation performance were investigated (Table 1). Compound **4** has good thermal stability with an onset decomposition temperature (T_{dec}) of

Table 1: Physicochemical and energetic properties of compound **4** compared with lead azide.

Property	**4**	$Pb(N_3)_2$
Formula	$C_6K_2N_{10}O_{10}$	PbN_6
M [g mol^{-1}]	450.3	291.3
T_{dec} [°C][a]	229	315
Ω_{CO} [%][b]	10.66	−11.0
N [%][c]	31.1	28.9
$N+O$ [%][d]	66.6	28.9
ρ [g cm^{-3}][e]	2.039	4.800[f]
IS [J][g]	2	2.5–4
FS [N][h]	20	0.1–1
ΔH_f [kJ mol^{-1}][i]	110.1	450.1
T_{det} [K][j]	3858.3	3353
νD [m s^{-1}][k]	8138	5877
P [GPa][l]	30.1	33.4

[a] Decomposition temperature (onset temperature at a heating rate of 5 °C min^{-1}). [b] Oxygen balance assuming the formation of CO. [c] Nitrogen content. [d] Nitrogen and oxygen content. [e] Density, measured with a gas pycnometer (25 °C). [f] Ref. [4]. [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.

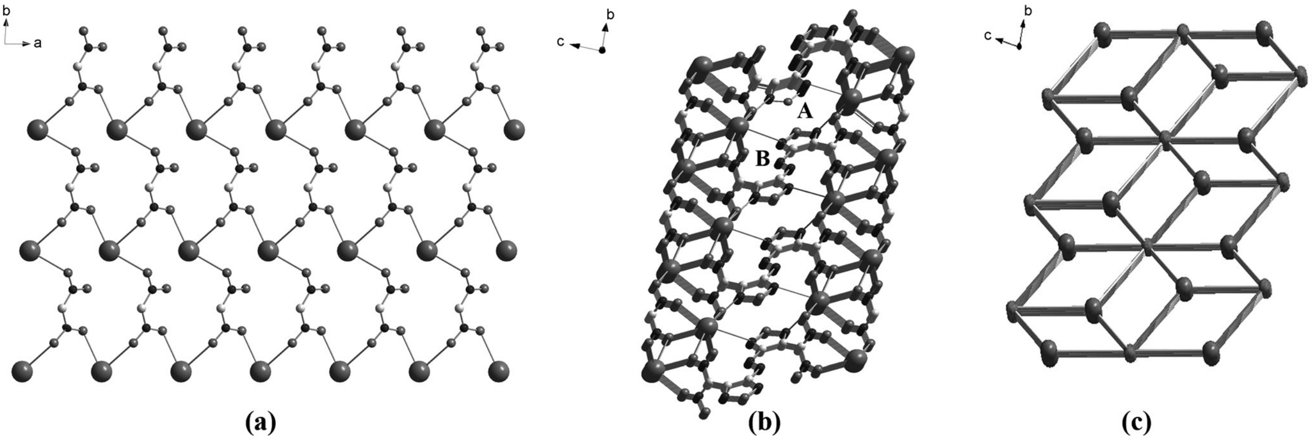


Figure 2. a) A 2D layer (*ab* plane) formed by dinitromethyl moieties and K ions. b) The full 3D framework of **4** along the *a* axis. c) A schematic representation of the topology, in which the dinitromethylazofurazan ligands are represented by small spheres and the K ions are represented by large spheres.

229 °C. The impact and friction sensitivity are 2 J and 20 N, respectively. With a calculated heat of formation of 110.1 kJ mol^{-1} and a measured density (2.039 g cm^{-3}), the detonation performance was calculated by using EXPLO5 v6.01.[15] The detonation velocity and pressure are 8138 m s^{-1} and 30.1 GPa, respectively. In addition, the oxygen balance of **4** is 10.66 %, whereas the content of oxygen and nitrogen is 66.6 %.

In summary, we have designed and synthesized a new 3D nitrogen-rich energetic MOF, potassium 4,4′-bis(dinitromethyl)-3,3′-azofurazanate (**4**), comprising an azofurazan moiety, dinitromethyl groups, and a nontoxic potassium ion. Compound **4** exhibits excellent thermal stability (T_d = 229 °C), good detonation performance, and sensitivity to external stimuli with an impact sensitivity of 2 J and a friction sensitivity of 20 N. Considering all the properties, **4** appears to be a very promising primary explosive.

Experimental Section

Caution**:** Although we have not experienced any difficulties in synthesizing and handling these compounds, they are potentially dangerous explosives. Proper protective precautions must be used.

4,4′-Bischlorohydroximoyl-3,3′-azofurazan (**2**): Compound **1**[12] (2.16 g, 10 mmol) was suspended in 30 mL ethanol, and 50 % aqueous hydroxylamine (1.65 g, 25 mmol) was added. After stirring for 30 min at room temperature, the solvent was removed and the remaining solid was washed with water and dried in air. Then the solid (2.8 g) was dissolved in a mixture of concentrated HCl (30 mL) and water (40 mL), and the solution was cooled to 0 °C. A solution of sodium nitrite (1.75 g, 25 mmol) in 10 mL water was added while keeping the temperature below 0 °C. The reaction mixture was stirred for 2 h at the same temperature. The solid was collected by filtration, washed with ice-water, and dried in air to give **2** as a yellow solid (1.96 g, 61 %). $T_m = 168$ °C. $T_d = 180$ °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 13.73$ ppm (s, 2 H). ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 160.7$, 146.9, 123.3 ppm. IR (KBr): $\tilde{\nu}$ =3344, 3029, 1697, 1614, 1546, 1479, 1384, 1267, 1237, 1032, 942, 887, 677, 610, 567 cm^{-1}. Elemental analysis calcd (%) for $C_6H_2Cl_2N_8O_4$ (321.04): C 22.45, H 0.63, N 34.90; found: C 22.68, H 0.56, N 35.48 %.

Potassium 4,4′-bis(dinitromethyl)-3,3′-azofurazanate (**4**): A suspension of **2** (1.96 g, 6.1 mmol) in $CHCl_2$ (20 mL) was added dropwise to a stirred mixture of 100 % HNO_3 (5 mL) and trifluoroacetic acid anhydride (8.8 mL) at 0 °C. The mixture was allowed to warm slowly to room temperature and stirred for 2 h. It was poured into ice water (60 mL) and extracted with $CHCl_2$ (3 × 30 mL). The organic phases were combined, washed with water and brine, dried over magnesium sulfate, and then concentrated under vacuum to provide the intermediate **3** as a yellow oil. Compound **3** was dissolved in methanol (20 mL), and a solution of potassium iodide (2.02 g, 12.2 mmol) in methanol (30 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature. The precipitate formed was collected by filtration and washed with cold water (5 mL), then methanol (5 mL), and ethyl ether (10 mL) to give **4** (0.92 g, 33.5 %) as an orange solid. $T_d = 229$ °C. ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta =$ 162.1, 139.9, 121.9 ppm. IR (KBr): $\tilde{\nu}$ =1746, 1630, 1557, 1500, 1463, 1398, 1225, 1145, 1067, 1001, 922, 820, 748, 698 cm^{-1}. Elemental analysis calcd (%) for $C_6K_2N_{10}O_{10}$ (450.32): C 16.00, H 0.00, N 31.10; found: C 16.36, H 0.17, N 30.36 %. Impact sensitivity (IS) = 2 J; friction sensitivity (FS) = 20 N.

Acknowledgements

This work was supported by the Office of Naval Research (N00014-12-1-0536) and the Defense Threat Reduction Agency (HDTRA 1-11-1-0034).

Keywords: detonation properties · energetic materials · metal–organic frameworks · primary explosives · X-ray diffraction

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 5565–5567
Angew. Chem. **2016**, *128*, 5655–5657

[1] a) R. Matyas, J. Pachman, *Primary Explosives*, Springer, Heidelberg, **2013**; b) T. Brinck, *Green Energetic Materials*, Wiley, Hoboken, **2014**; c) T. M. Klapötke, N. Mehta, *Propellants Explos. Pyrotech.* **2014**, *39*, 7–8.

[2] a) J. Sabatini, K. Oyler, *Crystals* **2015**, *6*, 5; b) J. P. Agrawal, R. D. Hodgson, *Organic Chemistry of Explosives*, Wiley, New York, **2007**.

[3] T. M. Klapötke, D. G. Piercey, N. Mehta, K. D. Oyler, M. Jorgensen, S. Lenahan, J. S. Salan, J. W. Fronabarger, M. D. Williams, *Z. Anorg. Allg. Chem.* **2013**, *639*, 681–688.

[4] D. Fischer, T. M. Klapötke, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172–8175; *Angew. Chem.* **2014**, *126*, 8311–8314.

[5] D. Fischer, T. M. Klapötke, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2015**, *54*, 10299–10302; *Angew. Chem.* **2015**, *127*, 10438–10441.

[6] C. He, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2016**, *55*, 772–775; *Angew. Chem.* **2016**, *128*, 782–785.

[7] a) J. Qin, J. Zhang, M. Zhang, D. Du, J. Li, Z. Su, Y. Wang, S. Pang, S. Li, Y. Lan, *Adv. Sci.* **2015**, *2*, 1500150; b) S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang, S. Pang, *Angew. Chem. Int. Ed.* **2013**, *52*, 14031–14035; *Angew. Chem.* **2013**, *125*, 14281–14285; c) M. H. V. Huynh, M. D. Coburn, T. J. Meyer, M. Wetzler, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10322–10327.

[8] a) Q. Zhang, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2014**, *53*, 2540–2542; *Angew. Chem.* **2014**, *126*, 2574–2576; b) J. Zhang, J. M. Shreeve, *Dalton Trans.* **2016**, *45*, 2363–2368; c) S. Zhang, Q. Yang, X. Liu, X. Qu, Q. Wei, G. Xie, S. Chen, S. Gao, *Coord. Chem. Rev.* **2016**, *307*, 292–312.

[9] a) H. Zhang, M. Zhang, P. Lin, V. Malgras, J. Tang, S. M. Alshehri, Y. Yamauchi, S. Du, J. Zhang, *Chem. Eur. J.* **2016**, *22*, 1141–1145; b) Y. Feng, X. Liu, L. Duan, Q. Yang, Q. Wei, G. Xie, S. Chen, X. Yang, S. Gao, *Dalton Trans.* **2015**, *44*, 2333–2339; c) X. Liu, W. Gao, P. Sun, Z. Su, S. Chen, Q. Wei, G. Xie, S. Gao, *Green Chem.* **2015**, *17*, 831–836.

[10] L. Zhai, X. Fan, B. Wang, F. Bi, Y. Li, Y. Zhu, *RSC Adv.* **2015**, *5*, 57833–57841.

[11] a) V. Thottempudi, H. Gao, J. M. Shreeve, *J. Am. Chem. Soc.* **2011**, *133*, 6464–6471; b) V. Thottempudi, J. M. Shreeve, *J. Am. Chem. Soc.* **2011**, *133*, 19982–19992; c) Y. Tang, C. He, H. Gao, J. M. Shreeve, *J. Mater. Chem. A* **2015**, *3*, 15576–15582.

[12] P. W. Leonard, D. E. Chavez, P. F. Pagoria, D. A. Parrish, *Propellants Explos. Pyrotech.* **2011**, *36*, 233–239.

[13] Y. Fan, B. Wang, Y. Zhou, S. Jia, H. Huo, *Chinese J. Energ. Mater.* **2009**, *17*, 385–388.

[14] CCDC 1448205 (**4**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[15] M. Sućeska, Brodarski Institute, Zagreb, Croatia, EXPLO5 v6.01, **2013**.

Received: February 9, 2016