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High-energy-density Materials Incorporating 4,5-Bis(dinitromethyl)-Furoxanate and 4,5-Bis(dinitromethyl)-3-oxy-furoxanate

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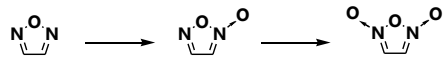
Abstract: Furoxan and its derivatives have been extensively favored in the field of energetic materials. The synthesis of 3-oxy-furoxan is extremely challenging. In this work, we successfully structurally immobilized 3-oxy-furoxanate in a heterometallic energetic MOF. Two furoxan-based energetic MOFs ($[Ag_2K_4(BDOFO)(BDFO)_2(H_2O)_6]_n$, $[K_2(BDFO)]_n$) and an energetic salt ($[(BDFO^{2-})(NH_2NH_3^+)_2(H_2O)]_n$ ($BDOFO^{2-}$ = 4,5- bis(dinitromethyl)-3-oxy-furoxanate, $BDFO^{2-}$ = 4,5-bis(dinitromethyl)-furoxanate) are reported, including synthesis, structure and energetic performance. This work would shed potential insights into the systematic investigation of detonation performance of 3-oxy-furoxan and its derivatives.

Keywords: Energetic MOFs/ 4,5-Bis(dinitromethyl)-3-oxy-furoxanate / 4,5-Bis(dinitromethyl)-furoxanate / Energetic performance/ Oxygen Balance

Energetic metal-organic frameworks (EMOFs) are a fascinating class of energetic materials which have already demonstrated potential as propellants, explosives and pyrotechnics because of their structural reinforcement, high thermal ability and lower sensitivity toward external stimuli. [1] The investigation and development of the nitrogen-rich energetic ligands is still a current research interest in the field of energetic materials.

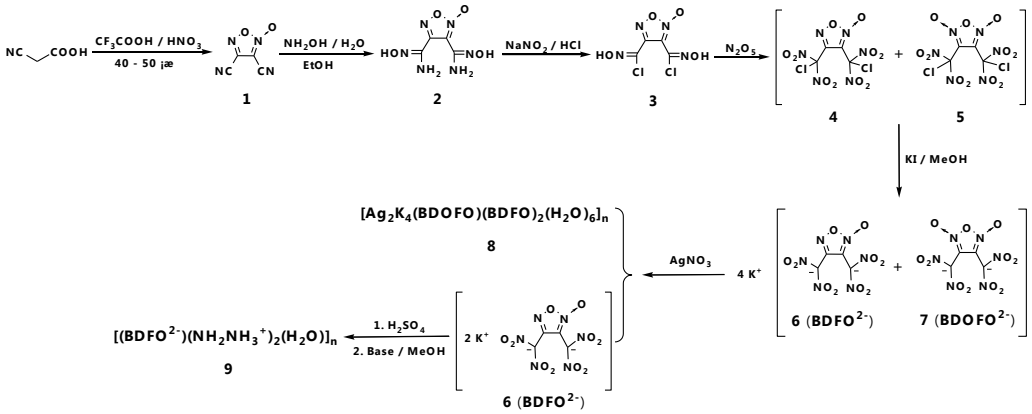
Furoxan and its derivatives are superior candidates for energetic materials and have been used to construct energetic MOFs because of their positive heat of formation and good oxygen balances (Scheme 1). [2] Theoritical calculations show that 3-oxy-furoxan has a higher heat of formation, better oxygen balance, and improved detonation performance compared to furazan and furoxan. It

is conceivable that 3-oxy-furoxan-based energetic materials could have outstanding detonation performance.



	Furazan	Furoxan	3-oxy-furoxan
Heat of formation (kJ mol^{-1}):	147.3	144.7	155.5
Detonation velocity (m s^{-1}):	6479.8	7521.1	8259.2
Detonation pressure (GPa):	16.4	23.3	28.9
Oxygen balance (CO_2, %):	-91.3	-55.8	-31.3
Oxygen balance (CO, %):	-45.7	-18.6	0

Scheme 1. Comparison of properties of furazan, furoxan and 3-oxy-furoxan.



Scheme 2. Syntheses of compounds **BDFO** and **BDOFO**.

Recently, Shreeve and co-workers synthesized potassium 4,5-bis(dinitromethyl)furoxanate possessing high sensitivity and remarkable detonation performance. [3] We have simultaneously performed the synthesis of furoxan/3-oxy-furoxan and their derivatives, as shown in Scheme 2. In contrast to Shreeve's work, where trifluoroacetic anhydride and 100 % HNO_3 was used, we chose N_2O_5 as the nitration reagent due to its strong oxidizing potential under mild reaction conditions.[4] Herein, we present the experimental procedure for the synthesis of 4,5-bis(dinitromethyl)-furoxanate and 4,5-bis(dinitromethyl)-3-oxy-furoxanate, the structures of intermediate product 4,5-bis(chlorodinitromethyl)furoxan (**4**), two furoxan-based energetic MOFs ($[K_2(BDFO)]_n$ (**6**) and $[Ag_2K_4(BDOFO)(BDFO)_2(H_2O)_6]_n$ (**8**)) and an energetic salt ($[(BDFO^{2-})(NH2NH_3^+)_2(H_2O)]_n$ (**9**)) ($BDOFO^{2-}$ = 4,5-bis(dinitromethyl)-3-oxy-furoxanate, $BDFO^{2-}$ = 4,5-bis(dinitromethyl)-furoxanate). Most importantly, we have structurally

characterized the first example of a 3-oxy-furoxan by trapping it as its metal salt in the form of a MOF.

Compounds **1**-**3** were synthesized according to previous methods (Scheme 2).[3,4] Similarly, **4** and **5** were obtained using N_2O_5. Compound **4** was structurally characterized by single crystal X-ray diffraction, even though it was unstable upon standing. Treatment of **4** and **5** with KI in methanol, however, we were unable to obtain X-ray quality crystals upon repeated efforts. Accidentally, to the aqueous solution system of the mixture **6** and **7** which $AgNO_3$ aqueous solution was added, a few pale yellow crystals **8** yielded at room temperature. To our surprise, there is only one peak in the filtered solution checked by HPLC, and fortunately, compound **6** crystallized from the solution above. It is followed that, to the solution of **6** acidified with 50 % H_2SO_4 which hydrazine was added, an energetic salt **9** was produced with a yield of 61.5 % (based on **6**).

Compounds **4**, **6**, **8** and **9** have been characterized by IR, elemental analysis, ^{13}C NMR spectroscopy and single crystal X-ray diffraction. The crystal data and structure refinement details of compounds **4**, **6**, **8** and **9** are summarized in Table S5, and the selected bond lengths and angles data are presented in Table S6. The X-ray diffraction analysis has confirmed the structure of compound **4** (Fig. S1)**.**

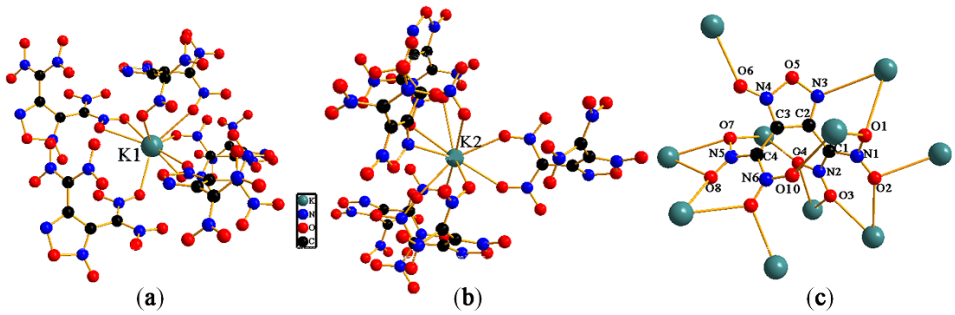


Fig. 1. a) Coordination environment of K1(I) ion, b) coordination environment of K2(I) ion, c) coordination model of ligand of **6**. (Hydrogen atoms are omitted for clarity).

Compound **6** crystallizes in the monoclinic *P*2(1)/c space group with two independent K(I) ions and one $BDFO^{2-}$ ligand in the asymmetric unit.[3] The K1(I) ion is coordinated to eight oxygen atoms (O1, O6, O7, O8, O9, O10, O8A, O9A) from five different $BDFO^{2-}$ ligands (Fig. 1a). The K2(I) ion is coordinated to eight oxygen atoms and one nitrogen atom (O1, O2, O3, O4, O7, O2A,

O3A, O4A, N3) from five different $BDFO^{2-}$ ligands (Fig. 1b). The bond lengths of K-O and bond angles of O-K-O are within 2.6562(16) Å-3.1530(16) Å and 41.68(4) °-173.26(5) °, respectively. The $BDFO^{2-}$ ligands (Fig. 1c) and K(I) ions are linked each other to generate a 3D EMOF (Fig. S2).

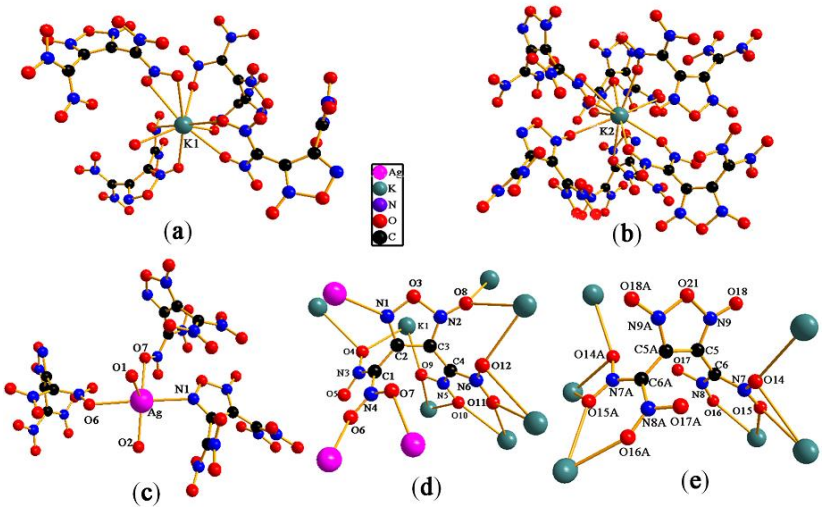


Fig. 2. a) Coordination environment of K1(I) ion, b) coordination environment of K2(I) ion, c) coordination environment of Ag(I) ion, d) coordination model of $BDFO^{2-}$ ligand, e) coordination model of $BDOFO^{2-}$ ligand of **8**. (Hydrogen atoms are omitted for clarity).

Compound **8** is a 3D heterometallic metal-organic framework and crystallizes in the orthorhombic *I*ba2 space group with an asymmetric unit consisting of two crystallographically independent Ag(I) ions, four K(I) ions, one $BDOFO^{2-}$ ligand, two $BDFO^{2-}$ ligands and six coordinated water molecules. K1(I) ion is nine-coordinated with nine oxygen atoms from three $BDFO^{2-}$ ligands (O4, O8, O9, O10, O11, O12), one $BDOFO^{2-}$ ligand (O14, O15) and one water molecule (O13) (Fig. 2a). K2(I) ion is coordinated to ten oxygen atoms from four $BDFO^{2-}$ ligands (O4, O8, O9, O10, O11, O12), two $BDOFO^{2-}$ ligands (O14, O15, O16) and one water molecule (O1) (Fig. 2b). The Ag1(I) ion is five-coordinated to four oxygen atoms from two $BDFO^{2-}$ ligands (O6, O7), and two water molecules (O1, O2), and one nitrogen atom from one $BDFO^{2-}$ ligand (N1) (Fig. 2c). The bond lengths of K-O and Ag-O in compound **8** are in the range of 2.701(11) Å-3.252(12) Å and 2.161(11) Å-2.479(11) Å, respectively. And the bond angles of O-K-O and O-Ag-O fall into the range of 42.2(3) °-177.5(3) ° and 90.0(4) °-156.6(6) °, respectively. The detailed bond lengths and bond angles are listed in Table S6 in Supporting Information. The

$BDFO^{2-}$ ligand adopts both bridging and chelating coordination modes to K1, K2 and Ag atoms (Fig. 2d). The $BDOFO^{2-}$ ligand also features bridging and chelating coordination modes, but only to the K1 and K2 atoms (Fig. 2e) resulting in a compacted 3D framework (Fig. S3). Compound **9** crystallizes in the monoclinic *P*2(1)/c space group. The asymmetric unit is composed of one $BDFO^{2-}$ anion, two $NH_2NH_3^+$ cations and one water molecule. Both the $BDFO^{2-}$ and $NH_2NH_3^+$ ions participate in extensive hydrogen bonding, leading to a 3D hydrogen bond network that incorporates the free water molecules (Fig. 3).

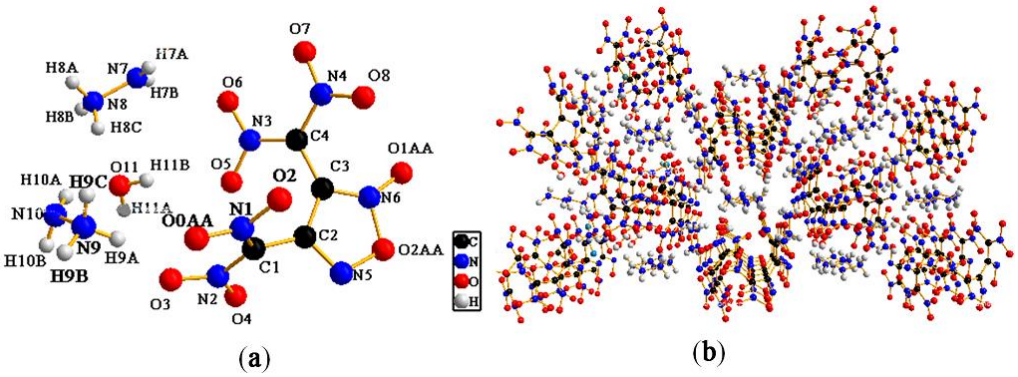


Fig. 3. a) The asymmetric unit of **9** showing the atom-numbering scheme, b) 3D structural network of **9**.

In **6** and **8**, the $BDFO^{2-}$ ligand exhibits different coordination modes to the metal ions generating 3D structural frameworks, which has a crucial effect on the thermal stability and detonation performance.

By comparing the structures of **6** and **8**, it is reasonable to conclude that compound **7** has been formed by oxidation with N_2O_5 followed by metathesis with KI. Since compound **4** is the precursor for **6**, we may deduce that compound **5** is the precursor to compound **7**. This is the first report that 3-oxy-furoxan was structurally characterized by trapping it as its anion in a metal complex. Quantum chemical calculations were carried out using the Gaussian 09 (Revision A.02) program package and visualized by GaussView 5.05,[5] and the detonation properties were evaluated by the commercial program EXPLO5 v6.01.[6] The calculated parameters of the related energetic compounds are listed in Table 1. As shown in Table 1, the calculated detonation pressures of the compounds range from 27.3 GPa (**6**) to 38.4 GPa (**9**). The calculated detonation velocities are from 7759 m s^{-1} (**6**) to 9294.7 m s^{-1} (**9**). Noteworthily, the calculated detonation properties of hydrazinium salt (**9**) are higher than those of potassium

4,4'-bis(dinitromethyl)-3,3'-azofurazanate (P = 30.1 GPa, D = 8138 m s^{-1}) [7]. And the impact and friction sensitivities of **9** are less insensitive than **6** and potassium 4,4'-bis(dinitromethyl)-3,3'-azofurazanate, possibly due to the extensive hydrogen-bonding interaction between the cations and anions.

Table 1. Calculated parameters of compounds **4**, **6**, **8** and **9.**

Compounds	**4**	**6**	**8**	**9**
Empirical formula	$C_4C_{l2}N_6O_{10}$	$K_2C_4N_6O_{10}$	$C_{12}H_{12}Ag_2K_4N_{18}O_{37}$	$C_4H_{12}N_{10}O_{11}$
M [a] (g mol^{-1})	363.0	370.3	1372.5	376.2
P [b] (g cm^{-3})	1.97	2.13	2.31	1.81
T_{dec} [c] (^oC)	67.8	218.9	231.3	120.8
Ω_{CO} [d] (%)	30.9	21.3	18.7	12.3
Ω_{CO2} [e] (%)	13.2	4.3	4.7	-4.47
N[f] (%)	23.2	22.7	18.40	37.24
N+O[g] (%)	67.23	65.9	61.5	84.03
Δ_fH_m [h] (kJ mol^{-1})	-55.6	-421.0	--	180.6
P [i] (GPa)	30.3	27.3	--	38.4
D [j] (m s^{-1})	8057.2	7759.0	--	9294.7
IS[k] (J)	5	2	--	9
FS[l] (N)	76	5	--	170

[a] Molecular weight. [b] From X-ray diffraction. [c] Decomposition temperature. [d] Oxygen balance for $C_aH_bO_cN_d$: 1600(c-a-b/2)/M. [e] Oxygen balance for $C_aH_bO_cN_d$: 1600(c-2a-b/2)/M. [f] Nitrogen content. [g] Nitrogen and oxygen content. [h] Heat of formation. [i] Detonation velocity calculated with EXPLO5 V6.01.[6] [j] Detonation pressure calculated with EXPLO5 V6.01.[6] [k] Impact sensitivity. [l] Friction sensitivity.

In summary, we have trapped the anion of 3-oxy-furoxan in a heterometallic energetic MOF and characterized the complex by IR, elemental analysis, and X-ray crystallography. This finding provides insight in the search for new high energy densitiy materials. Future efforts will focus on the development of 3-oxy-furoxan based compounds.

Experimental Section

General caution: The related furazan-based compounds in this work are seriously hazardous materials and may explode under certain external conditions. The compound should be handled with proper safety precautions such as safety glasses, face shields, and plastic spatulas, particularly when they are prepared on a large scale.

The detailed synthetic processes of compounds **1**-**9** are depicted in Scheme 2 and described in Supporting Information.

Acknowledgements

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Table-of-Contents

3-oxy-furoxan was first caught in a hereometallic 3D energetic MOF, which would provide a ray of light in searching for High-energy-density-materials.