

## SYNTHESIS AND CRYSTAL STRUCTURE OF TRINUCLEAR POTASSIUM(I) COMPLEX WITH OXY-BRIDGED BIS(*GEM*-DINITRO)FURAZAN AND TRIAMINO GUANIDINIUM

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**ABSTRACT.** A furazan-based trinuclear potassium(I) complex derived from the oxy-bridged bis(*gem*-dinitro)furazan (OBNF) and triaminoguanidinium (TGA) units was synthesized and characterized by elemental analyses, nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. The single crystal X-ray structure of the complex has been determined. It revealed that the asymmetric unit contains two crystallographically independent OBNF<sup>2-</sup> anion, one triaminoguanidinium cation, three potassium cations (K<sup>+</sup>) and one crystallized water molecule. In the crystal structure, intra- and intermolecular hydrogen bonding interactions as well as weak  $\pi$ - $\pi$  stacking interactions were observed, which are beneficial to form the net-like structure.

**KEY WORDS:** Trinuclear potassium(I) complex, Oxy-bridged bis(*gem*-dinitro)furazan, Triaminoguanidinium, Crystal structure, X-ray diffraction

### INTRODUCTION

Owing to containing abundant C–N, C=N and N–O chemical bonds, furazan ring is an important kind unit for constructing energetic compound. Recently, furazan ring has attracted widely attention due to their high standard enthalpy of formation, high nitrogen content, high energy density, good thermal stability, and low melting point [1–6]. The combination of nitrogen-rich furazan ring with energetic group or backbones containing acidic protons could serve as anions to form energetic compounds. In this regard, compounds such as, nitramine or tetrazole-functionalized based furazan had been investigated and were found to have shown promising performance [7–12]. The *gem*-dinitro group has been reported as being an effective anion to construct *gem*-dinitro group containing energetic compounds, with the high value of density contribution of 1.759 g cm<sup>-3</sup> [13–15]. To the best of our knowledge, the way of introducing *gem*-dinitro group into furazan ring to construct energetic compound is an effective strategy for developing novel energy material. Thus, herein, we report the synthesis and structural characterization of a furazan-based trinuclear potassium(I) and its X-ray crystal structure is also investigated.

### EXPERIMENTAL

#### *Material and measurements*

All reagents, unless otherwise specified, were obtained from the J&K Chemical Co. LTD in analytical-grade. The material oxy-bridged bis(*gem*-dinitro)furazan (OBNF) was synthesized according to the reported procedure [15, 16].

NMR (<sup>1</sup>H and <sup>13</sup>C) were obtained on a Bruker AV500 NMR spectrometer and referred to tetramethylsilane (TMS). Chemical shifts were reported in ppm and splitting patterns were designed as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broaden). Infrared spectra were obtained on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000–400 cm<sup>-1</sup>, using KBr pellets. Elemental analyses (C, H and N) were recorded on a VARI-EL-3 elemental analyzer.

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*Synthesis of dipotassium oxy-bridged bis (gem-dinitro)furazan (1)*

Potassium hydroxide (0.224 g, 4 mmol) was added to a solution of OBNF (0.724 g, 2 mmol) in 10 mL methanol. After stirring for 1 h at room temperature, 0.809 g (yield: 92.3%) yellow precipitate was filtered off. Analysis: found: C 16.34%, N 25.67%; calculated for  $C_6K_2N_8O_{11}$ : C 16.44%, N 25.57%. IR data ( $cm^{-1}$ , KBr): 1589, 1526, 1479, 1239, 1070, 997.  $^{13}C$  NMR (DMSO- $d_6$ , 125 MHz, ppm):  $\delta$  160.77, 142.31, 118.67.

*Synthesis of potassium triaminoguanidinium oxy-bridged bis(gem-dinitro)furazan (2)*

A solution of  $AgNO_3$  (0.085 g, 0.5 mmol) in 10 mL water was added to a solution of **1** (0.438 g, 1 mmol) in 10 mL water. After stirring for 0.5 h at room temperature, triaminoguanidinium chloride (0.070 g, 0.5 mmol) was added. The resulting mixture was stirred at 60 °C for an additional 1 h. After removal of the  $AgCl$  precipitate, the solution was evaporated *in vacuo* and the target product (yellow crystals) was obtained (Yield: 60.1%). Analysis: found: C 16.16, H 0.75, N 32.35; calculated for  $C_{13}H_8K_3N_{22}O_{23}$ : C 16.30, H 0.84, N 32.18. IR data ( $cm^{-1}$ , KBr): 3464, 3369, 3321, 1671, 1540, 1479, 1389, 1325, 1238, 1141, 999, 963, 868, 823, 747.  $^1H$  NMR (500 MHz,  $d_6$ -DMSO, ppm):  $\delta$  8.59 (s, 3H, NH), 4.49 (s, 6H,  $NH_2$ ).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ , ppm):  $\delta$  161.1, 159.4, 142.6, 119.0.

Table 1. Crystallographic data and experimental details for potassium complex.

Formula	$C_{13}H_8K_3N_{22}O_{23}$
FW	957.71
Crystal shape/color	Block/yellow
Crystal size/mm	$0.35 \times 0.28 \times 0.16$
Crystal system	Monoclinic
Space group	$P2_1/c$
T/K	296 (2)
$a/\text{\AA}$	16.224 (2)
$b/\text{\AA}$	12.6924 (15)
$c/\text{\AA}$	16.2788 (19)
$\beta/\text{deg}$	97.442 (2)
$V/\text{\AA}^3$	3323.8 (7)
Z	4
$D_c, g\text{ cm}^{-3}$	1.914
$\mu/\text{mm}^{-1}$	0.54
$F(000)$	1924
$\theta$ Range, deg	1.3–25.0
Index ranges/ $h, k, l$	–18 19; –14 15; –18 19
Reflection collected	5152
Independent reflections ( $R_{int}$ )	0.066
Reflections with $I > 2\sigma(I)$	4084
Number of parameters	550
Goodness-of-fit on $F^2$	1.062
$R_1, wR_2$ ( $I > 2\sigma(I)$ ) <sup>a</sup>	0.081, 0.249
$R_1, wR_2$ (all data) <sup>a</sup>	0.0396, 0.0466
$\Delta\rho_{min}/\Delta\rho_{max}/e\text{\AA}^{-3}$	0.71, –0.73
CCDC No.	1012874

$${}^aR_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} \quad wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$$

Table 2. Selected bond lengths (Å) and angles (deg) for the potassium complex.

Bond length	d, Å	Bond length	d, Å	Bond length	d, Å
K1-O1	2.758(6)	K1-O3	2.772(6)	K1-O9	2.838(5)
K1-O22 <sup>i</sup>	2.885(5)	K1-O12 <sup>ii</sup>	2.889(5)	K1-O3 <sup>iii</sup>	2.967(6)
K1-O13 <sup>ii</sup>	2.991(6)	K1-O4 <sup>ii</sup>	3.027(5)	K1-N6 <sup>i</sup>	3.143(6)
K2-O2 <sup>iii</sup>	2.722(6)	K2-O20 <sup>iv</sup>	2.858(5)	K2-O10	2.868(5)
K2-O9	2.881(6)	K2-O19 <sup>iv</sup>	2.962(5)	K2-O22 <sup>i</sup>	3.030(5)
K2-O4 <sup>ii</sup>	3.165(6)	K3-O13 <sup>iv</sup>	2.691(5)	K3-O20	2.743(5)
K3-O8 <sup>iii</sup>	2.804(5)	K3-O14 <sup>iv</sup>	2.827(7)	K3-O11	2.912(7)
K3-O21	2.957(6)	K3-O10 <sup>iv</sup>	2.995(5)	K3-K2 <sup>iv</sup>	4.522(2)
Bond angle	$\omega$ , deg	Bond angle	$\omega$ , deg	Bond angle	$\omega$ , deg
O1-K1-O3	56.01(16)	O1-K1-O9	98.09(17)	O3-K1-O9	80.08(19)
O1-K1-O22 <sup>i</sup>	122.07(16)	O3-K1-O22 <sup>i</sup>	162.46(18)	O9-K1-O22 <sup>i</sup>	83.17(17)
O1-K1-O12 <sup>ii</sup>	113.93(17)	O3-K1-O12 <sup>ii</sup>	104.74(17)	O9-K1-O12 <sup>ii</sup>	144.49(15)
O22 <sup>i</sup> -K1-O12 <sup>ii</sup>	91.92(16)	O1-K1-O3 <sup>iii</sup>	128.86(16)	O3-K1-O3 <sup>iii</sup>	74.74(19)
O9-K1-O3 <sup>iii</sup>	57.35(15)	O22 <sup>i</sup> -K1-O3 <sup>iii</sup>	100.42(16)	O12 <sup>ii</sup> -K1-O3 <sup>iii</sup>	89.43(15)
O1-K1-O13 <sup>ii</sup>	70.90(16)	O3-K1-O13 <sup>ii</sup>	82.02(17)	O9-K1-O13 <sup>ii</sup>	162.07(16)
O22 <sup>i</sup> -K1-O13 <sup>ii</sup>	114.58(15)	O12 <sup>ii</sup> -K1-O13 <sup>ii</sup>	43.05(14)	O3 <sup>iii</sup> -K1-O13 <sup>ii</sup>	118.15(17)
O1-K1-O4 <sup>ii</sup>	168.00(17)	O3-K1-O4 <sup>ii</sup>	112.62(16)	O9-K1-O4 <sup>ii</sup>	82.48(15)
O22 <sup>i</sup> -K1-O4 <sup>ii</sup>	69.93(13)	O12 <sup>ii</sup> -K1-O4 <sup>ii</sup>	62.98(15)	O3 <sup>iii</sup> -K1-O4 <sup>ii</sup>	42.12(14)
O13 <sup>ii</sup> -K1-O4 <sup>ii</sup>	105.33(15)	O1-K1-N6 <sup>i</sup>	69.83(15)	O3-K1-N6 <sup>i</sup>	122.81(17)
O9-K1-N6 <sup>i</sup>	127.53(16)	O22 <sup>i</sup> -K1-N6 <sup>i</sup>	64.84(14)	O12 <sup>ii</sup> -K1-N6 <sup>i</sup>	80.04(15)
O3 <sup>iii</sup> -K1-N6 <sup>i</sup>	161.28(16)	O13 <sup>ii</sup> -K1-N6 <sup>i</sup>	63.09(15)	O4 <sup>ii</sup> -K1-N6 <sup>i</sup>	119.27(15)
O2 <sup>iii</sup> -K2-O20 <sup>iv</sup>	131.95(19)	O2 <sup>iii</sup> -K2-O10	68.76(18)	O20 <sup>iv</sup> -K2-O10	75.86(14)
O2 <sup>iii</sup> -K2-O9	84.35(18)	O20 <sup>iv</sup> -K2-O9	100.11(15)	O10-K2-O9	53.65(15)
O2 <sup>iii</sup> -K2-O19 <sup>iv</sup>	125.6(2)	O20 <sup>iv</sup> -K2-O19 <sup>iv</sup>	43.57(13)	O10-K2-O19 <sup>iv</sup>	111.42(15)
O9-K2-O19 <sup>iv</sup>	142.15(16)	O2 <sup>iii</sup> -K2-O22 <sup>i</sup>	94.74(18)	O20 <sup>iv</sup> -K2-O22 <sup>i</sup>	133.26(15)
O10-K2-O22 <sup>i</sup>	131.07(15)	O9-K2-O22 <sup>i</sup>	79.92(15)	O19 <sup>iv</sup> -K2-O22 <sup>i</sup>	115.20(15)
O2 <sup>iii</sup> -K2-O4 <sup>ii</sup>	156.84(18)	O20 <sup>iv</sup> -K2-O4 <sup>ii</sup>	67.81(13)	O10-K2-O4 <sup>ii</sup>	112.85(16)
O9-K2-O4 <sup>ii</sup>	79.43(15)	O19 <sup>iv</sup> -K2-O4 <sup>ii</sup>	76.37(16)	O22 <sup>i</sup> -K2-O4 <sup>ii</sup>	66.31(13)
O13 <sup>iv</sup> -K3-O20	113.94(17)	O13 <sup>iv</sup> -K3-O8 <sup>iii</sup>	85.45(16)	O20-K3-O8 <sup>iii</sup>	114.75(15)
O13 <sup>iv</sup> -K3-O14 <sup>iv</sup>	56.51(17)	O20-K3-O14 <sup>iv</sup>	160.02(19)	O8 <sup>iii</sup> -K3-O14 <sup>iv</sup>	83.3(2)
O13 <sup>iv</sup> -K3-O11	157.98(19)	O20-K3-O11	63.50(15)	O8 <sup>iii</sup> -K3-O11	115.93(17)
O14 <sup>iv</sup> -K3-O11	117.80(19)	O13 <sup>iv</sup> -K3-O21	124.11(18)	O20-K3-O21	53.99(15)
O8 <sup>iii</sup> -K3-O21	63.51(15)	O14 <sup>iv</sup> -K3-O21	145.8(2)	O11-K3-O21	73.57(18)
O13 <sup>iv</sup> -K3-O10 <sup>iv</sup>	72.88(16)	O20-K3-O10 <sup>iv</sup>	75.52(14)	O8 <sup>iii</sup> -K3-O10 <sup>iv</sup>	158.33(15)
O14 <sup>iv</sup> -K3-O10 <sup>iv</sup>	84.63(19)	O11-K3-O10 <sup>iv</sup>	85.64(17)	O21-K3-O10 <sup>iv</sup>	129.51(16)

Symmetry codes: (i)  $-x+1, y+1/2, -z+1/2$ ; (ii)  $-x+1, -y+2, -z$ ; (iii)  $-x+1, y-1/2, -z+1/2$ ; (iv)  $-x+1, -y+1, -z$ .

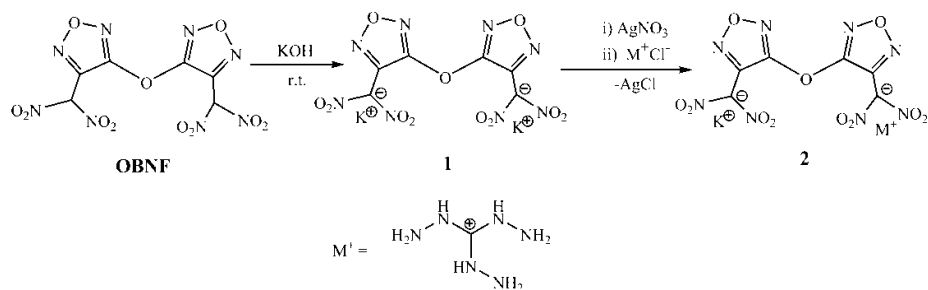
#### X-ray structure determination

Single crystal X-ray diffraction data were collected at 296(2) K on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Suitable crystal was affixed to the end of glass fibers using silicone grease and transferred to the goniostat. The unit cell parameters were obtained from SAINT; absorption corrections were performed with SADABS [17]. The structure was solved by direct methods and refined by the full-matrix least-squares method on  $F^2$  using the SHELXTL crystallographic software package [18]. The non-hydrogen atoms were refined anisotropically, hydrogen atoms were positioned geometrically (N-H = 0.86 Å) and were refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.20 U_{\text{eq}}(\text{N})$ . Crystallographic data and experimental details for potassium complex are summarized in Table 1. The selected bond lengths and angles of the potassium complex are given in Table 2.

## RESULTS AND DISCUSSION

*General*

The OBNF was synthesized according to the previously reported procedure [15] and further deprotonated and formed the divalent  $\text{OBNF}^{2-}$  in the presence of KOH with the yield of 92.3%. Then,  $\text{OBNF}^{2-}$  was reacted with  $\text{AgNO}_3$  aq., and the  $\text{K}^+$  was replaced by the  $\text{Ag}^+$ . Afterwards, the intermediate reacted with triaminoguanidinium chloride under  $60^\circ\text{C}$  to afford the potassium-containing complex. The obtained complex was confirmed by elemental analysis, IR, NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra. These preliminary measurements indicated that  $\text{OBNF}^{2-}$  anion and the second ligand triaminoguanidinium ( $\text{TAG}^+$ ) cation all coordinated to K ion center. Furthermore, the complex are soluble in methanol, ethanol, *N,N*-dimethylformide (DMF), dimethyl sulfoxide (DMSO) high polar solvents.



Scheme 1. Synthesis of the potassium(I) complex.

*IR spectra*

It was noted that the IR spectrum of the complex was consistent with the structure as determined by X-ray diffraction. The absorption bands at approximately 3464, 3369, 3321, 999, 963, 868, 823 and  $747\text{ cm}^{-1}$  are observed, which are similar to the complexes [15]. The absorption bands in the range of  $3500\text{--}3300\text{ cm}^{-1}$  are assigned to the symmetric N–H stretching vibrational models of the nitrogen-rich cations. Furthermore, peaks at 1671, 1540, 1479, 1389, 1325, 1238,  $1141\text{ cm}^{-1}$  are attributed to C=N and  $\text{NO}_2$  bonds vibrational models and peaks placed at 999, 963, 868, 823 and  $747\text{ cm}^{-1}$  can be assigned to C–N and K–O bond stretching vibrations model [7,19–21].

*NMR analysis*

As shown in Figure 1a, proton signal ( $\delta$  8.59) of compound 2 can be attributed to the –NH– in the cation triaminoguanidinium ( $\text{TAG}^+$ ), while another proton signal (4.49 ppm) could ascribe to – $\text{NH}_2$  of the  $\text{TAG}^+$ . And these two protons with a ratio of 1:2, indicating the  $\text{TAG}^+$  cation was existed in the compound 2. Furthermore, in  $^{13}\text{C}$  NMR spectra (Fig. 1b), three signals at 161.1, 142.7 and 119.0 ppm can attribute to O–C=N–, –N=CC( $\text{NO}_2$ ) $_2$  and C( $\text{NO}_2$ ) $_2$  of the  $\text{OBNF}^{2-}$  anion, which are close to the reported data [21]. It suggested that  $\text{OBNF}^{2-}$  anion existed in the complex. And another 159.4 ppm signal is related to the C(NHNH $_2$ ) $_3$  cation. It was noted that the  $^{13}\text{C}$  NMR signal of gem-dinitro group carbon (C( $\text{NO}_2$ )) at 119.0 ppm appeared at higher field compared to the ones in literature (129 to 132 ppm) [22–24], which resulted from the conjugation of negative charge throughout the aromatic rings [21].

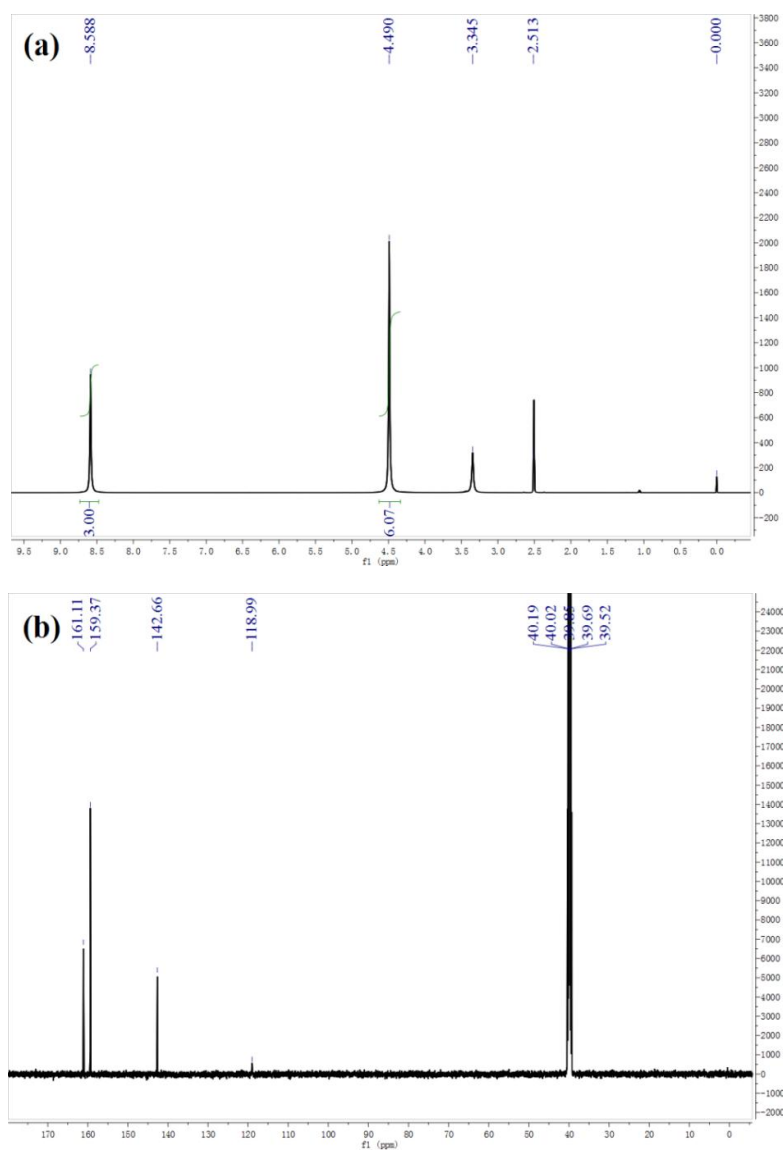


Figure 1.  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) spectra for the potassium(I) complex in  $\text{DMSO}-d_6$ .

#### Structure description of the complex

Complex **2** crystallizes in the monoclinic space group  $P2_1/c$  with calculated density of  $1.914 \text{ g cm}^{-3}$ . The asymmetric unit contains two crystallographically independent deprotonated  $\text{OBNF}^{2-}$  anion, one triaminoguanidinium ( $\text{TAG}^+$ ,  $\text{C}(\text{NHNH}_2)_2(\text{NHNH})^+$ ) cation, three potassium cation ( $\text{K}^+$ ) and one crystallized water molecule. As to the anion, the bridged oxygen atom is nearly coplanar with both furazan rings (torsion angle  $\text{O6-C3-C2-N3}$   $174.74^\circ$ ,  $\text{O6-C4-C5-N6}$   $179.184^\circ$ ,  $\text{O17-C9-C8-N11}$   $178.16^\circ$  and  $\text{O17-C10-C11-N14}$   $179.66^\circ$ ). The dihedral angle

between two furazan ring planes (defined by C2C3N4O5N3 and C5C4N5O7N6) between two furazan ring planes is  $33.48^\circ$ , while one (defined by C8C9N11O16N12 and C10C11N13O18N14) is only  $14.48^\circ$ , which are similar to the reported oxy-bridged furazan structures [15]. The length of the C–C bonds (C2–C3, C4–C5, C8–C9 and C10–C11) connecting gem-dinitro and furazan ring are 1.420, 1.426, 1.420 and 1.422 Å, respectively. These bond data are between C–C single bond (1.530 Å) and C=C double bond (1.320 Å) [25]. These might indicate conjugation of negative charge throughout the aromatic rings [15, 21].

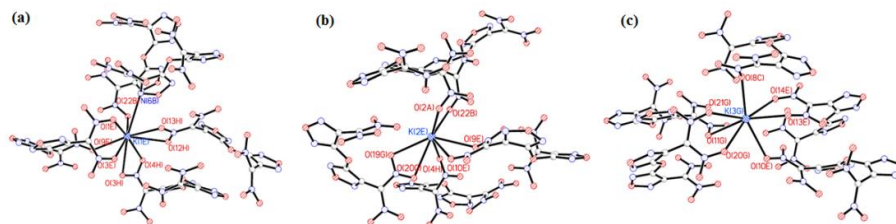


Figure 2. The coordination environments of K(1)<sup>+</sup> ion (a), K(2)<sup>+</sup> ion (b) and K(3)<sup>+</sup> ion (c) in the complex. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.

Table 3. Hydrogen bonding distances (Å) and bond angles (deg) for complex.

D-H...A	D-H, Å	H...A, Å	D...A, Å	D-H...A, deg
N17-H17...N21	0.86	2.53	2.818(11)	101
N19-H9A...N22	0.86	2.47	2.754(11)	100
N20-H20...N17	0.86	2.34	2.671(9)	103
N22-H22...N19	0.86	2.42	2.754(11)	104
N17-H17...O5 <sup>i</sup>	0.86	2.32	3.085(9)	149
N18-H18...O23 <sup>ii</sup>	0.86	2.06	2.912(11)	170
N19-H19B...O12 <sup>iii</sup>	0.86	2.53	3.215(9)	137
N19-H19B...N11 <sup>iii</sup>	0.86	2.46	2.911(9)	114
N20-H20...O22 <sup>iv</sup>	0.86	2.28	3.059(8)	151
N21-H21A...O23 <sup>ii</sup>	0.86	2.45	3.235(13)	153
N21-H21B...N12 <sup>v</sup>	0.86	2.38	3.156(10)	151
N21-H21B...N13 <sup>v</sup>	0.86	2.58	3.178(12)	127

Symmetry codes: (i)  $1-x, -1/2+y, 1/2-z$ ; (ii)  $-x, 1-y, -z$ ; (iii)  $1-x, 2-y, -z$ ; (iv)  $1-x, 1/2+y, 1/2-z$ ; (v)  $-1+x, 3/2-y, -1/2+z$ .

As shown in Figure 2, there are different coordination environment for the three potassium central ions. For the potassium cation (K(1)<sup>+</sup>), the potassium ion is nona-coordinated by eight nitro oxygen atoms (O(1), O(3), O(9), O(22)<sup>i</sup>, O(3)<sup>ii</sup>, O(4)<sup>ii</sup>, O(12)<sup>ii</sup>, O(13)<sup>ii</sup>) and furazan nitrogen atom (N(6)<sup>i</sup>) from the OBNF<sup>2-</sup> anion, and connects with five adjacent OBNF<sup>2-</sup> anions through eight K–O coordination bonds [K(1)–O(1), K(1)–O(3) and K(1)–O(9); K(1)–O(22)<sup>i</sup>; K(1)–O(3)<sup>ii</sup> and K(1)–O(4)<sup>ii</sup>; K(1)–O(12)<sup>ii</sup> and K(1)–O(13)<sup>ii</sup>] from four different OBNF<sup>2-</sup> anions, the bond distance are between 2.758 and 3.027 Å] and one K–N coordination bond [K(1)–N(6)<sup>i</sup> from one OBNF<sup>2-</sup> anion, 3.143 Å] (Figure 2a, Table 2). The atoms involved coordination formed a distorted tetradecahedron with potassium ion as coordinate center, atom N(6)<sup>i</sup> and O(3)<sup>ii</sup> in the axis position and other seven oxygen atoms at the equatorial plane (the bond angle of N(6)<sup>i</sup>–K(1)–O(3)<sup>ii</sup> is  $161.28^\circ$ ). For the potassium cation (K(2)<sup>+</sup>), the potassium ion is hepta-coordinated by seven nitro oxygen atoms (O(2)<sup>iii</sup>, O(22)<sup>i</sup>, O(19)<sup>iv</sup>, O(20)<sup>iv</sup>, O(20)<sup>iv</sup>, O(4)<sup>ii</sup>, O(9)

and O(10)) from  $\text{OBNF}^{2-}$  anions, and connects with five adjacent  $\text{OBNF}^{2-}$  anions through seven K–O coordination bonds [K(2)–O(2)<sup>iii</sup>; K(2)–O(22)<sup>i</sup>; K(2)–O(19)<sup>iv</sup> and K(2)–O(20)<sup>iv</sup>; K(2)–O(4)<sup>ii</sup>; K(2)–O(9) and K(2)–O(10) from five different  $\text{OBNF}^{2-}$  anions, the bond distance are between 2.722 and 3.165 Å] (Figure 2b, Table 2). Interestingly, it was observed that there exist a weak K–N coordinating bond [K(3)–N(17)<sup>i</sup>, 3.214(7) Å], which linked the central potassium cation and the second ligand TAG<sup>+</sup>. For the potassium cation (K(3)<sup>+</sup>), the potassium ion is hepta-coordinated by seven nitro oxygen atoms (O(8)<sup>iii</sup>, O(11), O(21)<sup>i</sup>, O(20), O(10)<sup>iv</sup>, O(13)<sup>iv</sup> and O(14)<sup>iv</sup>) from  $\text{OBNF}^{2-}$  anions, and connects with five adjacent  $\text{OBNF}^{2-}$  anions through seven K–O coordination bonds [K(3)–O(8)<sup>iii</sup>; K(3)–O(11); K(3)–O(21)<sup>i</sup> and K(3)–O(20); K(3)–O(10)<sup>iv</sup>; K(3)–O(13)<sup>iv</sup> and K(3)–O(14)<sup>iv</sup> from five different  $\text{OBNF}^{2-}$  anions, 2.743–2.957 Å] (Figure 1c, Table 2). The central atom involved coordination formed a distorted decahedron with potassium ion as coordinate center, atom O(8)<sup>iii</sup> and O(10)<sup>iv</sup> (the bond angle of N(6)<sup>i</sup>–K(1)–O(3)<sup>ii</sup> is 158.33°) in the axis position and other five atoms at the equatorial plane. It was noted that, (i) K(1)<sup>+</sup> linked the K(2)<sup>+</sup> via three bridge nitro atoms (O(22)<sup>i</sup> and O(4)<sup>ii</sup>), (ii) K(2)<sup>+</sup> linked the K(3)<sup>+</sup> via two bridge nitro atoms (O(10) and O(20)), (iii) K(1)<sup>+</sup> linked the K(3)<sup>+</sup> via one bridge nitro atoms (O(13)). Also, the weak K–O (3.215–3.402 Å) and K–N interaction (3.227–3.350 Å), and metal-metal K–K interaction [K(3)–K(2)<sup>iv</sup>, 4.522 Å], which were observed in the similar complex [15]. Furthermore, in the crystal structure of the resultant complex, four intramolecular hydrogen bonding N–H⋯N (N17–H17⋯N21, N19–H9A⋯N22, N20–H20⋯N17 and N22–H22⋯N19) interaction and eight intermolecular hydrogen bonding N–H⋯O (N17–H17⋯O5<sup>i</sup>, N18–H18⋯O23<sup>ii</sup>, N19–H19B⋯O12<sup>iii</sup>, N20–H20⋯O22<sup>iv</sup> and N21–H21A⋯O23<sup>ii</sup>), N–H⋯N (N19–H19B⋯N11<sup>iii</sup>, N21–H21B⋯N12<sup>v</sup>, N21–H21B⋯N13<sup>v</sup>) (Figure 3, Table 3) were existed, and stabilizes the TAG<sup>+</sup> and adjacent  $\text{OBNF}^{2-}$  unit. Besides hydrogen bonding interactions, the weak  $\pi$ – $\pi$  interactions (Table 3) between the adjacent furazan rings could be also observed, thus further formed the net-like structure.

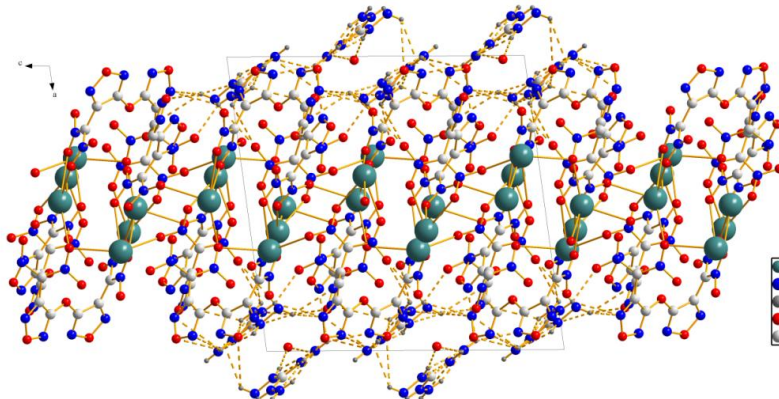


Figure 3. The diagram showing the intra- and intermolecular hydrogen bonding interaction in the complex viewed along the b axis.

Table 4.  $\pi$ – $\pi$  stacking interaction (Å, deg) for complex.

Ring(I)	Ring(J)	$\alpha$ , deg	DCC (Å)	CgI–prep, Å	CgI–prep, Å
Cg2	Cg3	15.7(4)	4.331(4)	3.236 (3)	3.848(3)
Cg2	Cg4	14.5(4)	4.320(4)	3.154(3)	3.174(3)

DCC = distance between ring centroids;  $\alpha$  = dihedral angle between planes I and J; CgI–prep = perpendicular distance of Cg(I) from ring J; Cg2, Cg3 and Cg4 for the complex are the centroids of furazan ring O7N5C4C5N6, O16N11C8C9N12 and O18N13C10C11N14.

## CONCLUSION

A furazan-based trinuclear potassium(I) complex derived from OBNF and TGA units has been prepared and structurally characterized single crystal X-ray diffraction method, as well as elemental analyses, NMR, IR spectroscopic technique. The symmetric unit contains two crystallographically independent OBNF<sup>2-</sup> anion, one triaminoguanidinium cation, three potassium cations (K<sup>+</sup>) and one crystallized water molecule. In the crystal structure, intra- and intermolecular hydrogen bonding interactions, weak  $\pi$ - $\pi$  stacking interactions were observed.

*Supplementary data.* The crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 1012874). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail for deposition: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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