



Effect of counter-ion on packing and crystal density of 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1H-tetrazol-1-olate) with five different cations

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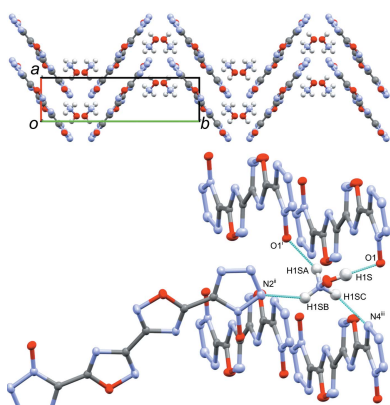
In energetic materials, the crystal density is an important parameter that affects the performance of the material. When making ionic energetic materials, the choice of counter-ion can have detrimental or beneficial effects on the packing, and therefore the density, of the resulting energetic crystal. Presented herein are a series of five ionic energetic crystals, all containing the dianion 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1H-tetrazol-1-olate), with the following cations: hydrazinium (**1**) ($2\text{N}_2\text{H}_5^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$), hydroxylammonium (**2**) $2\text{NH}_4\text{O}^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$ [Pagoria *et al.* (2017). *Chem. Heterocycl. Compd*, **53**, 760–778; included for comparison], dimethylammonium (**3**) ($2\text{C}_2\text{H}_8\text{N}^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$), 5-amino-1H-tetrazol-4-ium (**4**) ($2\text{CH}_4\text{N}_5^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}\cdot 4\text{H}_2\text{O}$), and aminoguanidinium (**5**) ($2\text{CH}_7\text{N}_4^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$). Both the supramolecular interactions and the sterics of the cation play a role in the density of the resulting crystals, which range from 1.544 to 1.873 Mg m^{-3} . In **5**, the tetrazolate ring is disordered over two positions [occupancy ratio 0.907 (5):0.093 (5)] due to a 180° rotation in the terminal tetrazole rings.

1. Chemical context

One of the critical parameters directly related to the performance of an energetic material, specifically its detonation velocity, is the density of the material (Ma *et al.*, 2014; Akhavan, 2011). This is an important consideration when designing energetic materials that incorporate counter-ions into their structures, since these counter-ions can, through supramolecular interactions, aid or disrupt effective packing of the molecule in question. Presented herein are the structures of a single energetic molecule, 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1H-tetrazol-1-olate), as salts of five different cations: hydrazinium (**1**), hydroxylammonium (**2**) (Pagoria *et al.*, 2017, included for comparison), dimethylammonium (**3**), 5-amino-1H-tetrazol-4-ium (**4**), and aminoguanidinium (**5**). As a result of the variety of cation structures and intermolecular interactions, each exhibits subtly different crystal packing, which affects the resulting density. The molecule of interest, however, only exhibits minor changes in bond distances depending on the cation.

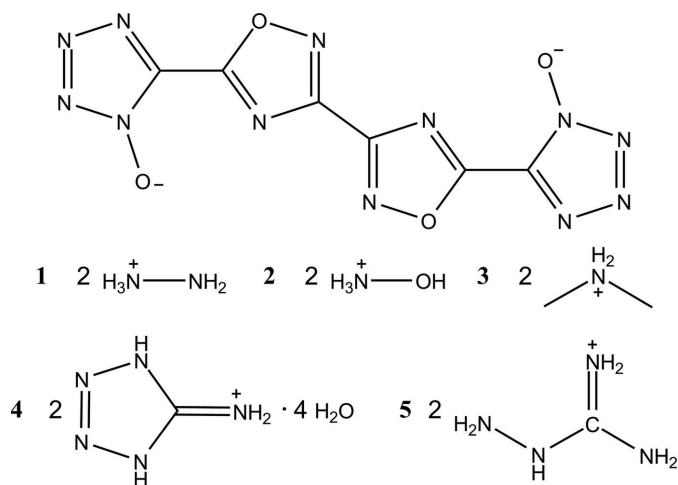
2. Structural commentary

The primary molecule, 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1H-tetrazol-1-olate), is comprised of four pentanuclear rings, with two 1,2,4-oxadiazole rings linked together through



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the 5-position carbon atom, and the tetrazol-1-olate rings linked at the 5-position carbon atom to each 1,2,4-oxadiazole ring at the 3-position carbon.



In each structure, the oxadiazole oxygen atoms are on opposite sides. For **1**, **2**, **3**, and **5** (Figs. 1–3, 5), the oxadiazole rings are coplanar with one another, with the N8–C9–C9′–N8′ torsion angles constrained to 180°. Only slight deviation from coplanarity is seen in **4** (Fig. 4), with the N8–C9–C11–N12 torsion angles measuring 179.34 (16)°. Coincidentally, **4** is the only structure in which the primary molecule does not reside on an inversion center. For all structures, except **3**, the tetrazolate ring is oriented such that the oxygen atoms of the oxadiazole and tetrazolate are on opposite sides, although **4** has a minor component of disorder [9.3 (4)%] in which one tetrazolate is flipped by 180°. The N4–C5–C6–N10 torsion angles for **1** [174.25 (13)°], **4** [179.82 (16)°], N20–C16–C14–N15 angle is 176.68 (16)°, and **5** [N4A–C5A–C6–N10, 174.8 (5)°] show only slight deflections from coplanar, while in **2** [168.63 (15)°], the deflection is more pronounced. In structure **3**, the N4–C5–C6–N10 dihedral angle is 2.38 (19)°, showing only a slight deviation from coplanarity, despite the proximity of the two electronegative oxygen atoms.

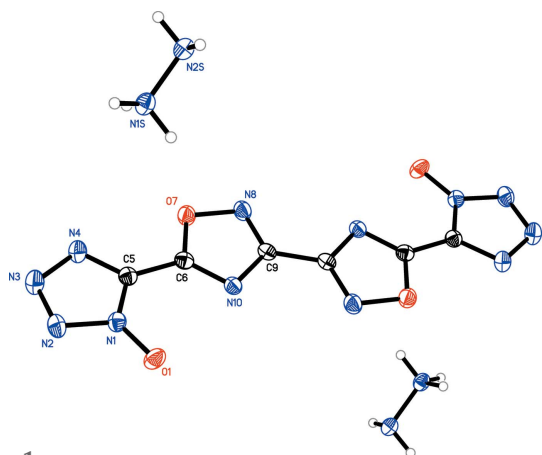


Figure 1
Molecular structure of **1**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

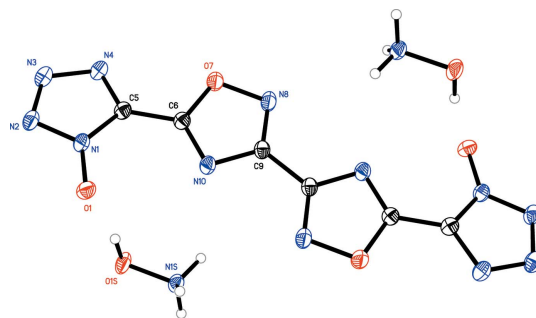


Figure 2
Molecular structure of **2**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

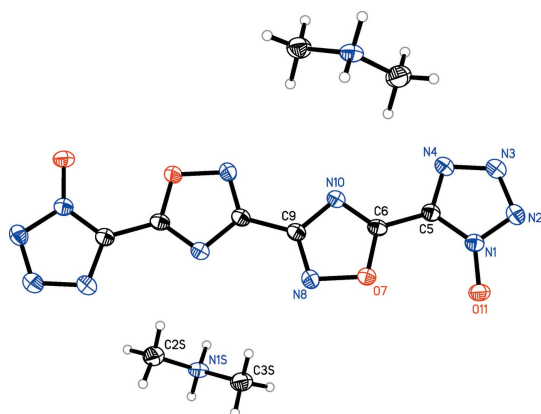


Figure 3
Molecular structure of **3**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

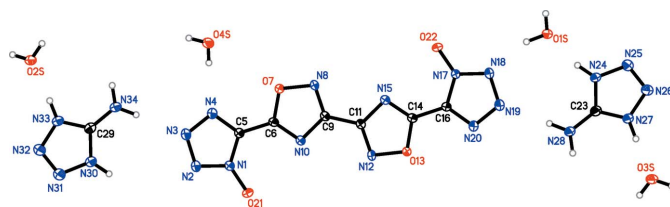


Figure 4
Molecular structure of **4**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

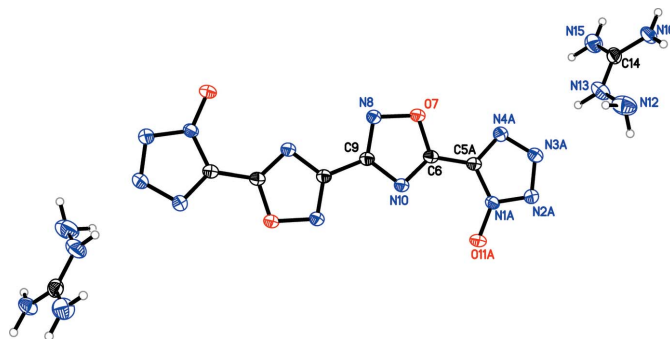


Figure 5
Molecular structure of the major disorder component of **5**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

In all five structures, the tetrazolate C–N and N–N bond distances [ranging from 1.328 (5) to 1.351 (2) Å and 1.3170 (17) to 1.3455 (16) Å, respectively] suggest a delocalized aromatic system rather than discrete single and double bonds (Allen *et al.*, 1987). The oxadiazole N–O, C–O, and C–N bond distances, however, suggest discrete single and double bonds. The N–O and C–O bonds range from 1.4033 (16) to 1.4115 (14) Å and 1.3391 (18) to 1.3468 (18) Å, respectively, suggesting single bonds between these atoms. The C–N bond opposite the oxygen atom ranges from 1.3671 (16) to 1.3755 (19) Å, also indicative of a single bond. The remaining C–N bonds range from 1.294 (2) to 1.309 (2) Å, typical for double bonds between these atoms. The central oxadiazole–oxadiazole C–C bond [ranging from 1.459 (3) to 1.465 (4) Å] and the C–C bonds linking the oxadiazole rings to the tetrazolate rings [ranging from 1.432 (2) to 1.447 (2) Å] are typical for C–C single bonds between non-fused heterocycles (Allen *et al.*, 1987).

Bond distances in the complex cations are typical for each. In **1**, the hydrazinium N–N bond distance of 1.4476 (16) Å matches the distance of 1.45 Å seen in hydrazinium chloride (Sakurai & Tomiie, 1952). In **2**, the hydroxylammonium N–O bond distance of 1.4087 (16) Å matches the distance of 1.41 Å seen for hydroxylammonium perchlorate (Dickens, 1969). In **3**, the dimethylammonium C–N distances of 1.4767 (18) and 1.4780 (17) Å are consistent, albeit on the low side, with those reported for dialkylammonium ions, on average 1.494 (16) Å (Allen *et al.*, 1987). In **4**, the bond distances of 5-amino-1*H*-tetrazol-4-ium are consistent with those seen in 5-amino-1*H*-tetrazol-4-ium nitrate [bond type, distances (reference distances)]: C–N_{amino}, 1.320 (2) and 1.314 (2) Å (1.308 Å); C–N_{ring}, 1.334 (2) to 1.338 (2) Å (1.334 to 1.342 Å); C–N(H)–N=N, 1.357 (2) to 1.366 (2) Å (1.363 to 1.366 Å); N(H)–N=N–N(H), 1.272 (2) and 1.269 (2) Å (1.268 Å; von Denffer *et al.*, 2005). In **5**, the bond distances seen for the aminoguanidinium cation are consistent with those seen in aminoguanidinium nitrate and are as follows [bond type, distances (reference distances)]: C–NH₂, 1.309 (3) and 1.320 (3) Å (1.312 and 1.320 Å); C–N(H)(NH₂), 1.337 (3) Å (1.328 Å); and N(H)–NH₂, 1.420 (3) Å (1.399 Å; Akella & Keszler, 1994).

3. Supramolecular features

Packing of the energetic molecules will be described in four terms, following the example in Ma *et al.* (2014): sheet-like (with all molecules parallel to one another), wavelike (with two molecular planes that are not parallel to one another, but without intermolecular crossing), crossing (same as wavelike but with intermolecular crossing), and mixing (with molecular planes that do not fit in the prior three categories).

Structure **1**, space group $P2_1/c$, packs in a wavelike pattern consisting of alternating columns of 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1*H*-tetrazol-1-olate) (dianion) with the N2–N3 bond of one dianion over the tetrazolate ring of the dianion in the neighboring column (Fig. 6*a*). Hydrazinium ions occupy the gaps between neighboring coplanar dianions along

Table 1
Hydrogen-bond geometry (Å, °) for **1**.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1S–H1SA···N2S ⁱ	0.939 (17)	2.015 (18)	2.9353 (16)	166.1 (14)
N1S–H1SB···O1 ⁱⁱ	0.904 (18)	2.007 (17)	2.7679 (15)	141.0 (14)
N1S–H1SC···N4 ⁱⁱⁱ	0.930 (18)	2.018 (18)	2.8778 (17)	153.0 (14)
N2S–H2SA···N3 ^{iv}	0.883 (18)	2.227 (18)	3.0778 (17)	161.6 (15)
N2S–H2SB···O1 ^v	0.882 (18)	2.071 (18)	2.8752 (15)	151.2 (15)

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

the *b*-axis, above the plane of the molecules. One hydrazinium forms a hydrogen-bonded network linking the neighboring intrasheet dianions through the tetrazolate oxygen, tetrazolate N4 atom, and the NH₃ portion of hydrazinium. Additionally, hydrogen bonds form between the NH₂ portion of hydrazin-

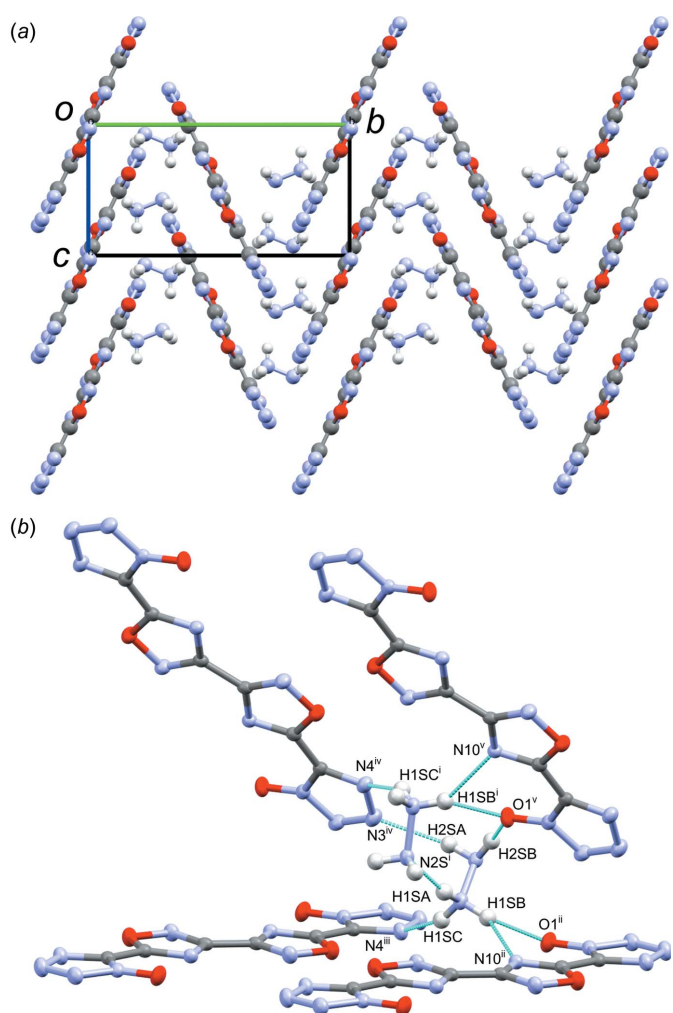


Figure 6
(*a*) Wavelike packing of **1** as seen down the *a*-axis, showing the opposing columns of the dianion with hydrazinium occupying gaps between the columns, and (*b*) view highlighting the hydrogen-bonding network (intermolecular contacts) between the dianions and hydrazinium cations, and between the two hydrazinium cations. [Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 2, -y + 2, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$].

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1S—H1S···O1	0.90 (2)	1.70 (2)	2.5880 (15)	169 (2)
N1S—H1SA···O1 ⁱ	0.89	2.02	2.8234 (17)	149
N1S—H1SB···N2 ⁱⁱ	0.89	2.35	2.9713 (19)	127
N1S—H1SC···N4 ⁱⁱⁱ	0.89	2.10	2.9425 (19)	157

Symmetry codes: (i) $x - 1, y, z$; (ii) $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x, y, z + 1$.

ium, the tetrazolate oxygen atom, and the tetrazolate N3 atom of neighboring dianions. An additional hydrogen bond connects the NH₃ of one hydrazinium with the NH₂ portion of the symmetry-related hydrazinium ion (Fig. 6b, Table 1). Intermolecular π – π stacking is limited in this structure, with tetrazolate–oxadiazole centroid_{N1–N4/C5}–centroid_{C6/O7/N8/C9/N10} distances of 4.06 (2) and 4.01 (2) Å. The tetrazolate oxygen atom forms an anion– π interaction with the oxadiazole ring of a neighboring dianion, with an O1-to-centroid_{C6/O7/N8/C9/N10} close contact of 2.98 (2) Å at an O1–centroid_{C6/O7/N8/C9/N10}–O7 angle of 92.3 (2)° (Schottel, *et al.*, 2008).

Structure **2**, space group $P2_1/c$, packs in a similar wavelike pattern as **1**; however, the N2–N3 bond of one dianion does not interact with the ring of neighboring dianions (Fig. 7a). Additionally, the opposing columns are staggered with respect to one another. The hydroxylammonium cations occupy the space formed where three dianion columns meet, above the

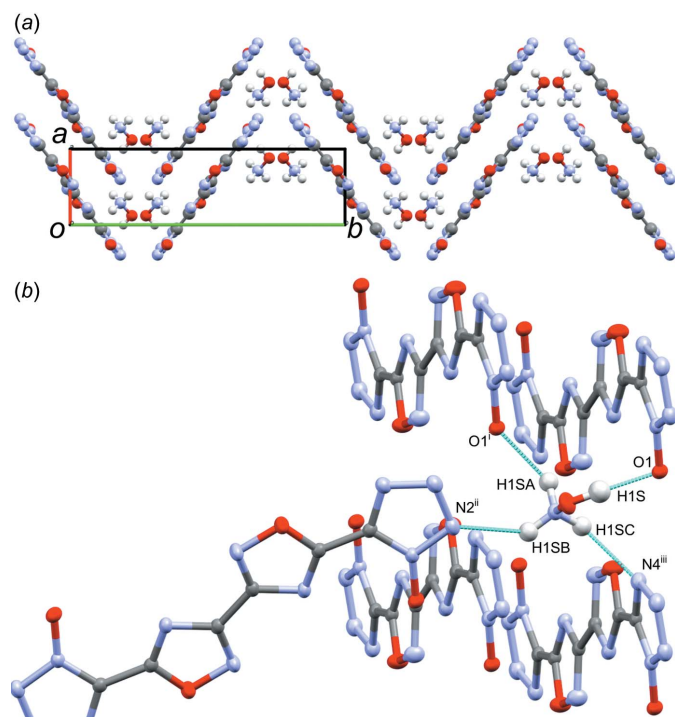


Figure 7
(a) Wavelike packing of **2** as seen down the *c*-axis, showing the opposing columns of dianion with hydroxylammonium occupying the space between the columns, and (b) view highlighting the hydrogen-bonding network (intermolecular contacts) between hydroxylammonium cation and the dianions. [Symmetry codes: (i) $x - 1, y, z$; (ii) $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x, y, z + 1$.]

Table 3
Hydrogen-bond geometry (Å, °) for **3**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1S—H1SA···O11 ⁱ	0.91	2.01	2.8118 (14)	146
N1S—H1SB···O11 ⁱⁱⁱ	0.91	1.85	2.7524 (14)	169

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

dianion planes. The arrangement of the dianions in the peaks and troughs of the packing is dictated by the hydrogen bonds between the hydroxylammonium hydroxyl group and the tetrazolate oxygen atom, and those between the hydroxylammonium NH₃ group and O1, N2, and N4 of three symmetry-related dianions (Fig. 7b, Table 2). Unlike **1**, there is a strong π – π [centroid_{C6/O7/N8/C9/N10}–centroid_{N1–N4/C5} distance 3.36 (2) Å, centroid_{N1–N4/C5}–centroid_{C6/O7/N8/C9/N10}–O7 angle, 80 (2)°] interaction between the tetrazolate and oxadiazole rings. Additionally, the tetrazolate oxygen atom does not participate in an anion– π interaction with the oxadiazole ring due to the stronger π – π interaction. The oxadiazole rings of neighboring dianions are far apart, at a centroid_{C6/O7/N8/C9/N10}–centroid_{C6/O7/N8/C9/N10} distance of 4.26 (2) Å and a centroid_{C6/O7/N8/C9/N10}–centroid_{C6/O7/N8/C9/N10}–N10 angle of 50 (2)°, suggesting minimal π – π interaction.

Structure **3**, space group $P\bar{1}$, packs in a sheet-like pattern (Fig. 8a), with the dianion stacked in a staggered arrangement, with the tetrazolate ring of one dianion over the central oxadiazole–oxadiazole C–C bond of the dianions above and

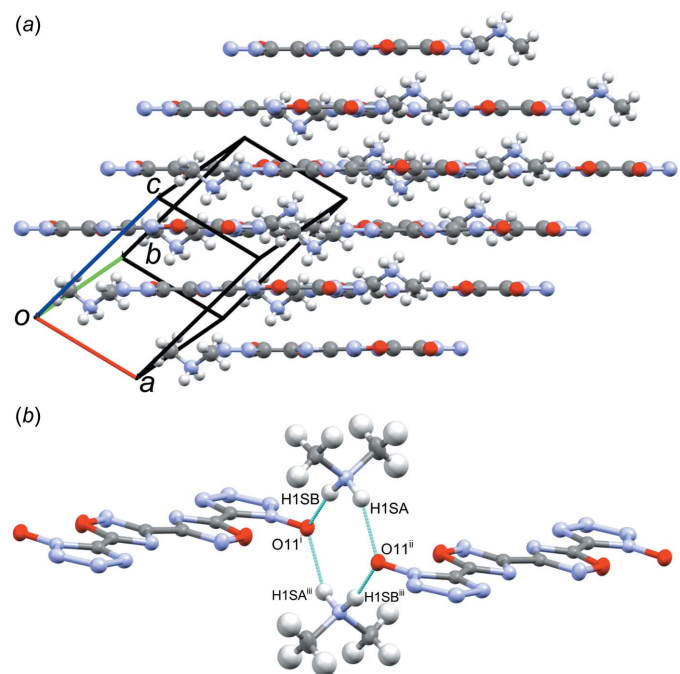


Figure 8
(a) Sheet-like packing of **3** as viewed approximately perpendicular to the (021) plane, showing the layers of dianion and associated dimethylammonium cations, and (b) view highlighting the hydrogen-bonding network (intermolecular contacts) between dimethylammonium cations and the dianions. [Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, -y, -z + 1$; (iii) $1 - x, -y, -z$.]

Table 4
Hydrogen-bond geometry (Å, °) for **4**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N24—H24···O1S	0.88	1.76	2.6267 (18)	169
N27—H27···O3S	0.88	1.74	2.6241 (19)	177
N28—H28A···N19	0.88	2.18	3.054 (2)	176
N28—H28B···O22 ⁱ	0.88	1.99	2.8656 (19)	172
N30—H30···O4S ⁱⁱ	0.88	1.75	2.605 (2)	165
N33—H33···O2S	0.88	1.78	2.6544 (19)	173
N34—H34A···N3	0.88	2.20	3.080 (2)	174
N34—H34B···O21 ⁱⁱⁱ	0.88	2.01	2.8882 (19)	175
O1S—H1SA···N20 ^{iv}	0.83 (3)	1.99 (3)	2.8030 (19)	170 (2)
O1S—H1SB···N18	0.87 (2)	1.94 (2)	2.7758 (19)	160 (2)
O2S—H2SA···N12 ⁱⁱⁱ	0.81 (2)	2.39 (2)	3.0906 (18)	144 (2)
O2S—H2SB···N10 ⁱⁱⁱ	0.81 (3)	2.19 (2)	2.9038 (18)	148 (2)
O3S—H3SA···N8 ⁱ	0.81 (2)	2.33 (2)	3.0397 (19)	147 (2)
O3S—H3SB···N15 ⁱ	0.82 (3)	2.21 (3)	2.8915 (19)	141 (2)
O4S—H4SA···N4	0.79 (3)	2.03 (3)	2.817 (2)	177 (3)
O4S—H4SB···N2 ⁱⁱⁱ	0.81 (3)	2.02 (3)	2.789 (2)	157 (3)

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z - \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x, y - \frac{1}{2}, -z - \frac{1}{2}$.

below. The oxadiazole ring resides over the tetrazolate–oxadiazole C—C bond in the dianions above and below. The void space between the dianion columns is occupied by dimethylammonium ions, located within the plane of the molecules in an up–down arrangement. Two dimethylammonium ions are positioned between the sheets, forming hydrogen bonds between the NH₂ group and the tetrazolate oxygen atoms of dianions in neighboring sheets (Fig. 8*b*, Table 3). The tetrazolate ring engages in a staggered π – π interaction

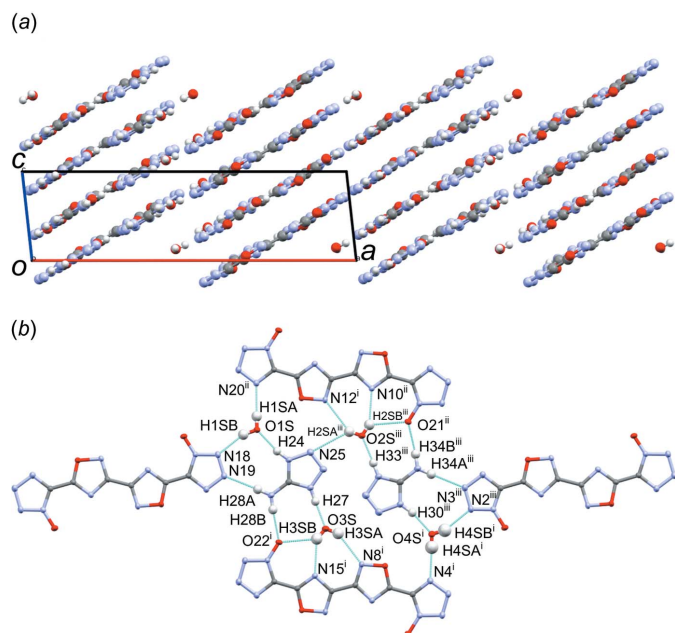


Figure 9
(a) Sheet-like packing of **4** as seen down the *b*-axis, showing the extended sheets containing both the dianion and the associated coplanar cations and solvent water, and (b) view highlighting the extensive in-plane hydrogen-bonding network between 5-aminotetrazolium, the surrounding dianions, and incorporated water molecules (intermolecular contacts). [Symmetry codes: (i) $-x, y + \frac{1}{2}, -z - \frac{1}{2}$; (ii) $-x, y - \frac{1}{2}, -z - \frac{1}{2}$; (iii) $x - 1, y, z - 2$.]

Table 5
Hydrogen-bond geometry (Å, °) for **5**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N12—H12B···N4A ⁱ	0.88 (1)	2.50 (1)	3.314 (4)	155 (3)
N13—H13···N3A ⁱⁱ	0.88	2.08	2.870 (3)	149
N13—H13···N4A ⁱⁱ	0.88	2.65	3.405 (4)	144
N15—H15A···O11A ⁱⁱⁱ	0.88	2.19	2.954 (3)	145
N15—H15B···N2A ^{iv}	0.88	2.24	3.112 (4)	170
N16—H16A···O11A ⁱⁱⁱ	0.88	2.18	2.949 (2)	146
N16—H16A···N10 ⁱⁱⁱ	0.88	2.29	2.926 (2)	129
N16—H16B···N8 ^v	0.88	2.32	3.079 (2)	145

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

with the oxadiazole rings of the neighboring dianion, at centroid_{C6/O7/N8/C9/N10}–centroid_{N1–N4/C5} distances of 3.51 (2) and 3.99 (2) Å (the latter distance to the inversion-related oxadiazole of the same dianion).

Structure **4**, space group $P2_1/c$, packs in the sheet-like pattern consisting of extended sheets containing the dianion, cations, and incorporated water (Fig. 9*a*). The 5-amino-1*H*-tetrazol-4-ium cations and water molecules surround each dianion, isolating the dianion from other dianions within the sheets. Between the sheets, the dianion only interacts with another dianion *via* one terminal tetrazolate ring, with the oxygen atom of the tetrazolate over the C—C bond between the tetrazolate and oxadiazole rings. Within each sheet, there is extensive hydrogen bonding between the dianions, 5-amino-1*H*-tetrazol-4-ium, and incorporated water molecules, isolating the dianions from one another in the sheet plane (Fig. 9*b*, Table 4). The N1-tetrazolate interacts with the symmetry-related N1-tetrazolate of a neighboring molecule through a π – π interaction, with a centroid_{N1–N4/C5}–centroid_{N1–N4/C5} distance of 3.69 (2) Å [N–centroid_{N1–N4/C5}–centroid_{N1–N4/C5} angle 62.0 (2)°]. The C11-oxadiazole engages in a π – π interaction with its symmetry equivalent as well, at a centroid_{C11/N12/O13/C14/N15}–centroid_{C11/N12/O13/C14/N15} distance of 3.93 (2) Å [centroid_{C11/N12/O13/C14/N15}–centroid_{C11/N12/O13/C14/N15}–O13 angle 57.6 (2)°, second centroid and O13 of the same dianion]. A π – π interaction is also seen between the N30-tetrazolium ring and its symmetry equivalent, at a centroid_{C29/N30–N33}–centroid_{C29/N30–N33} distance of 3.69 (2) Å [centroid_{C29/N30–N33}–centroid_{C29/N30–N33}–N31 angle 57.3 (2)°, second centroid and N31 of the same cation]. Additionally, there are two anion– π interactions, the first between O21 and the N1-tetrazolate of a neighboring dianion, and the second between O21 and the C6-oxadiazole, with an O21–centroid_{N1–N4/C5} distance of 3.33 (2) Å [O21–centroid_{N1–N4/C5}–N2 angle 95.8 (2)°] and O21–centroid_{C6/O7/N8/C9/N10} 3.02 (2) Å [O21–centroid_{C6/O7/N8/C9/N10}–C6 angle 76.3 (2)°].

Structure **5**, space group $P2_1/n$, packs in a mixing pattern, with columns containing stacked sheets consisting of the dianion coplanar with two aminoguanidinium cations (Fig. 10*a*). Neighboring columns of sheets are rotated by 67° with respect to one another as a result of the hydrogen bonding of the amino group of the cation with the oxygen atom of a neighboring oxadiazole ring. In fact, it is the

hydrogen-bonding interaction between the amino group of the aminoguanidinium cation and the oxygen atom of the oxadiazole that directs the mixing-type packing seen in the crystal structure. The planar portion of the aminoguanidinium cation interacts *via* hydrogen bonds from the unsubstituted guanidinium amines to the tetrazolate oxygen atom, oxadiazole N8, and symmetry-related oxadiazole N10 atoms of one dianion, and to the tetrazolate N2 atom of a neighboring dianion (Fig. 10*b*, Table 5). Additionally, the substituted guanidinium amine and its amine group interact with neighboring dianions through the tetrazolate N3 atoms, causing the deviation from sheet-like packing. There is limited π - π interaction between the oxadiazole and tetrazolate rings of neighboring dianions, with a centroid_{C6/O7/N8/C9/N10}-centroid_{N1A-N4A/C5A} distance of 3.59 (2) Å [centroid_{C6/O7/N8/C9/N10}-centroid_{N1A-N4A/C5A}-N1A angle 65.4 (2)°].

As demonstrated above, it is the hydrogen-bonding networks that establish the crystal packing exhibited in each

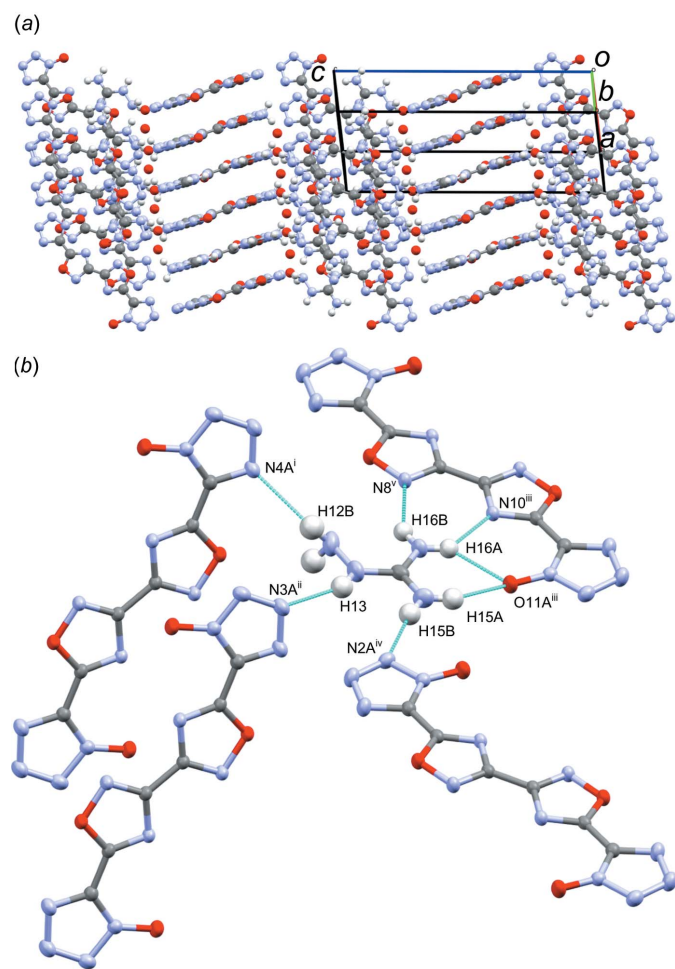


Figure 10
 (a) Mixing-type packing of **5** as viewed approximately perpendicular to the (110) plane, and (b) view highlighting the hydrogen bonding between the dianions and aminoguanidinium cations (intermolecular contacts, major dianion disorder component shown). [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $x - 1, y - 1, z$; (v) $x, y + 1, z$.]

Table 6
 Crystal densities of each structure.

Structure ID	Cation	Density (g cm ⁻³)
1	hydrazinium	1.694
2	hydroxylammonium	1.873
3	dimethylammonium	1.544
4	5-amino-1 <i>H</i> -tetrazol-4-ium	1.701
5	aminoguanidinium	1.673

example, with π - π and anion- π interactions occurring if packing allows. As shown in Table 6, the densities of the crystals increase in the order **3** < **6** < **1** < **5** < **2**. Unsurprisingly, the dimethylammonium, with minimal hydrogen bonding, non-interacting substituents, and a poor steric match for the dianion, is the least dense of the structures shown. Aminoguanidinium, despite significant hydrogen bonding, exhibits a lower density as well, likely due to the directionality of the hydrogen-bond donors, which directs packing of the dianions into less efficient arrangements. Hydrazinium benefits from extensive hydrogen bonding, but the orientation of the hydrazinium directs the dianions into slightly less efficient packing than the hydroxylammonium cation, preventing the staggering of the columns that allows for improved space occupation. The 5-amino-1*H*-tetrazol-4-ium cation, with the second-highest density, packs very efficiently, in extended sheets with extensive hydrogen bonding, losing out to the hydroxylammonium cation likely only due to the included water molecules needed to fill in gaps between the dianions and cations. Hydroxylammonium exhibits the most efficient, highest-density packing due to the directing influence and strong hydrogen-bond donating ability of the hydroxyl group, which forms a short hydrogen bond and directs the columns into a staggered arrangement, fitting the dianions slightly closer together at the point where neighboring columns meet. The range of densities, from 1.544 to 1.873 g cm⁻³, shows the significant effect that matching the hydrogen-bonding abilities and sterics of the counter-ion to the primary energetic ion has on efficient packing and, by extension, the expected performance of these ionic energetics.

4. Database survey

A search of the CSD (Version 5.38 with one update; Groom *et al.*, 2016) yields no results for structures containing 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1*H*-tetrazol-1-olate). A search using 5-[3-(1,2,4-oxadiazole)]-1*H*-tetrazolate also yields no results. Searching for the ring fragments separately yielded 443 structures for 1,2,4-oxadiazole and 127 structures for tetrazol-1-olate. The closest structures to those presented herein are dimers between similar ring fragments. A search for each of the cations yields the following results: 196 structures containing hydrazinium, 99 structures containing hydroxylammonium, 1,583 structures containing dimethylammonium, 2,230 structures containing ammonium, 17 structures containing 5-amino-1*H*-tetrazol-4-ium, and 130 structures containing aminoguanidinium.

5. Synthesis and crystallization

The synthesis pathway is illustrated in Fig. 11. The synthesis and crystallization of compound **2**, and the precursors 3,3'-bis(1,2,4-oxadiazole)-5,5'-dichloroxime (**6**) and 5,5'-(3,3'-bis(1,2,4-oxadiazole)-5,5'-diyl)bis(1-hydroxytetrazole) (**7**), have been described previously (Pagoria *et al.*, 2017).

Compound **1**: Dihydrate **8** (0.15 g, 0.44 mmol) was added to a 20 ml vial with water (1.5 ml) and a stir bar. Hydrazine hydrate (45 ml, 0.93 mmol) was added to the reaction mixture and heated until dissolved. Stirring was discontinued, the stir bar was removed, and the solution was allowed to cool slowly providing crystals of **1**.

Compound **3**: In a round-bottom flask, fitted with a drying tube, was suspended chloroxime **6** (967 mg, 3.3 mmol) in dimethylformamide (DMF) (10 ml, anhydrous), which was then cooled in an ice-water bath. Sodium azide (472 mg, 7.26 mmol) was added in portions with stirring, and the reaction was allowed to warm to room temperature. Additional DMF (10 ml) was added to the creamy mixture, and after 1.5 h, the solids went into solution. At this point, complete formation of the diazidoxime was assumed, and cyclization to **1** proceeded as follows. A 1:1 mixture of diethyl ether/dioxane was added to the reaction mixture (100 ml total volume, anhydrous), and the solution was cooled to 273 K with an ice bath. HBr or Cl₂ gas was bubbled into the reaction at which time the temperature increased to 298 K. Gas was added until the reaction temperature returned to approximately 278 K, and the vessel was then stoppered and allowed to stir for 22 h. The voluminous, white precipitate that formed (hygroscopic dimethylammonium bromide) was separated by

vacuum filtration, and the filtrate was allowed to evaporate from a crystallizing dish. Upon evaporation, a white solid (**3**) in a yellow oil remained. The solid was separated from the oil by vacuum filtration (535 mg). **3** was crystallized by heating in minimal water and slow cooling.

Compound **4**: Dihydrate **7** (0.15 g, 0.44 mmol) was added to a 20 ml vial with water (1.5 ml) and a stir bar. 5-Aminotetrazole (0.10 g, 1.2 mmol) was added to the mixture, which was then heated with stirring until dissolved. Stirring was discontinued, the stir bar was removed, and the solution was allowed to cool slowly providing crystals of **4**.

Compound **5**: Dihydrate **7** (0.15 g, 0.44 mmol) was added to a 20 ml vial with water (1.5 ml) and a stir bar. Aminoguanidinium H₂CO₃ (0.24 g, 1.8 mmol) was added to the mixture, which was then heated with stirring until dissolved. During dissolution, gas evolved, the solution became clear, followed by the formation of a tan precipitate. Heating was continued until complete dissolution, followed the removal of the stir bar, and slow cooling to provide crystals of **5**.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. In **5**, the tetrazolate ring (N1, N2, N3, N4, C5, O1) is disordered over two positions (*A* and *B*) due to a 180° rotation in the terminal tetrazole rings. The disorder has the relative ratio of 90.7 (5):9.3 (5). CCDC deposition numbers are as follows: **1**, CCDC 1567779; **2**, CCDC 1567780; **3**, CCDC 1567783; **4**, CCDC 1567784; **5**, CCDC 1567804.

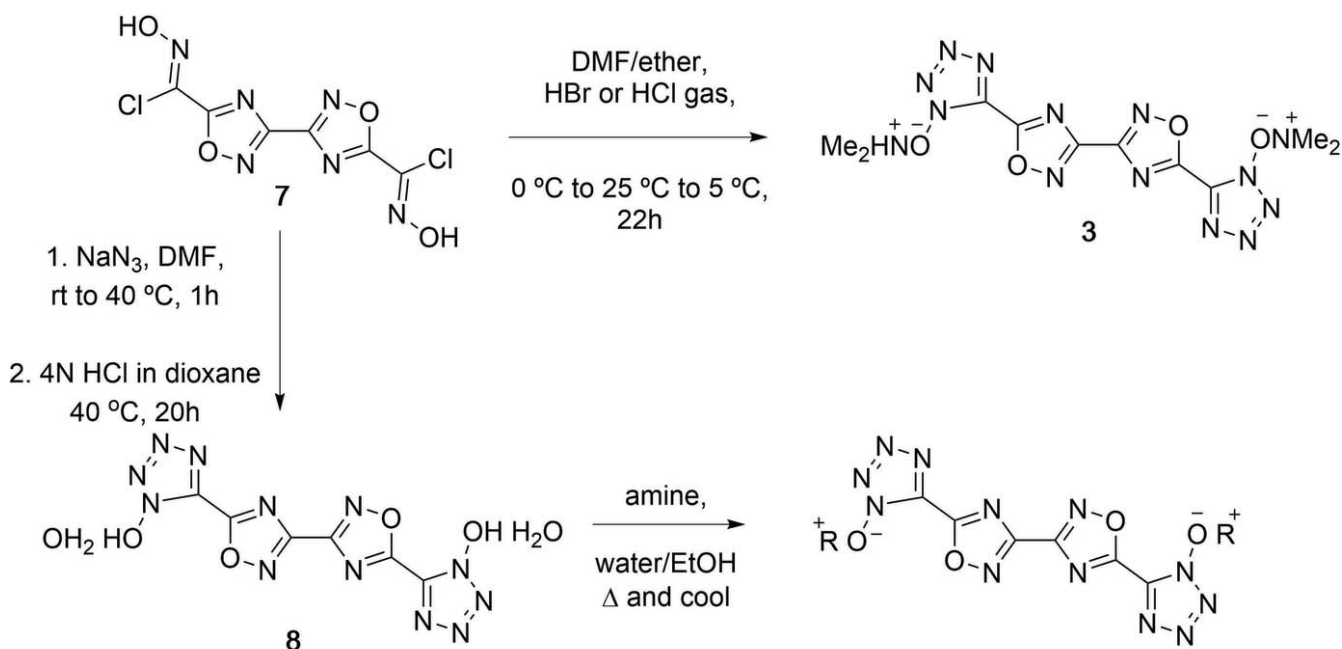


Figure 11
Scheme depicting synthesis pathways for the included structures.

Table 7
Experimental details.

	1	2	3
Crystal data			
Chemical formula	2N ₂ H ₅ ⁺ ·C ₆ N ₁₂ O ₄ ²⁻	2NH ₄ O ⁺ ·C ₆ N ₁₂ O ₄ ²⁻	2C ₂ H ₈ N ⁺ ·C ₆ N ₁₂ O ₄ ²⁻
<i>M_r</i>	370.30	372.26	396.37
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150	296	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.7660 (7), 13.6716 (13), 6.8655 (7)	5.1011 (9), 18.494 (3), 7.0044 (13)	6.0946 (6), 8.5197 (8), 9.2814 (9)
α , β , γ (°)	90, 95.237 (3), 90	90, 92.624 (2), 90	68.259 (3), 75.957 (3), 74.816 (3)
<i>V</i> (Å ³)	725.89 (12)	660.1 (2)	426.28 (7)
<i>Z</i>	2	2	1
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.14	0.17	0.12
Crystal size (mm)	0.16 × 0.15 × 0.02	0.33 × 0.19 × 0.02	0.18 × 0.12 × 0.04
Data collection			
Diffractometer	Bruker SMART APEXII CCD	Bruker SMART APEXII CCD	Bruker SMART APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)	Multi-scan (<i>SADABS</i> ; Bruker, 2014)	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.978, 0.997	0.948, 0.997	0.978, 0.995
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	6871, 1487, 1305	5834, 1358, 1152	4131, 1737, 1490
<i>R</i> _{int}	0.021	0.027	0.018
(sin θ/λ) _{max} (Å ⁻¹)	0.628	0.628	0.625
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.081, 1.04	0.034, 0.096, 1.08	0.032, 0.085, 1.04
No. of reflections	1487	1358	1737
No. of parameters	133	122	129
No. of restraints	0	0	0
H-atom treatment	Only H-atom coordinates refined	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.32, -0.22	0.23, -0.26	0.27, -0.24
<hr/>			
	4		5
Crystal data			
Chemical formula	2CH ₄ N ₅ ⁺ ·C ₆ N ₁₂ O ₄ ²⁻ ·4H ₂ O		2CH ₇ N ₄ ⁺ ·C ₆ N ₁₂ O ₄ ²⁻
<i>M_r</i>	548.36		454.39
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>		Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	150		150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	24.783 (2), 12.7081 (11), 6.8396 (6)		7.9458 (4), 5.5586 (2), 20.6066 (9)
α , β , γ (°)	90, 96.289 (1), 90		90, 97.647 (2), 90
<i>V</i> (Å ³)	2141.1 (3)		902.05 (7)
<i>Z</i>	4		2
Radiation type	Mo <i>K</i> α		Mo <i>K</i> α
μ (mm ⁻¹)	0.15		0.14
Crystal size (mm)	0.28 × 0.04 × 0.04		0.42 × 0.11 × 0.08
Data collection			
Diffractometer	Bruker SMART APEXII CCD		Bruker SMART APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)		Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.960, 0.994		0.944, 0.989
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	18508, 4274, 3489		7786, 1844, 1633
<i>R</i> _{int}	0.027		0.020
(sin θ/λ) _{max} (Å ⁻¹)	0.621		0.626
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.126, 1.14		0.045, 0.134, 1.06
No. of reflections	4274		1844
No. of parameters	367		206
No. of restraints	0		63
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement		H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.37, -0.32		0.74, -0.24

Computer programs: *APEX2* (Bruker, 2010), *SAINT* and *XPREP* (Bruker, 2014), *SHELXTL* (Sheldrick, 2008) and *SHELXL2016* (Sheldrick, 2015).

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supporting information

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Effect of counter-ion on packing and crystal density of 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1*H*-tetrazol-1-olate) with five different cations

Ian D. Giles, Alan J. DeHope, Nathaniel B. Zuckerman, Damon A. Parrish and Philip F. Pagoria

Computing details

For all structures, data collection: *APEX2* (Bruker, 2010); cell refinement: *APEX2* (Bruker, 2010); data reduction: *SAINTE* (Bruker, 2014) and *XPREP* (Bruker, 2014); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Bis(hydrazinium) 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1*H*-tetrazol-1-olate) (1)

Crystal data

$2\text{N}_2\text{H}_5^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$
 $M_r = 370.30$
 Monoclinic, $P2_1/c$
 $a = 7.7660$ (7) Å
 $b = 13.6716$ (13) Å
 $c = 6.8655$ (7) Å
 $\beta = 95.237$ (3)°
 $V = 725.89$ (12) Å³
 $Z = 2$

$F(000) = 380$
 $D_x = 1.694$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2894 reflections
 $\theta = 5.3\text{--}52.6^\circ$
 $\mu = 0.14$ mm⁻¹
 $T = 150$ K
 Plate, colorless
 $0.16 \times 0.15 \times 0.02$ mm

Data collection

Bruker SMART APEXII CCD
 diffractometer
 Radiation source: fine focus sealed tube
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2014)
 $T_{\min} = 0.978$, $T_{\max} = 0.997$
 6871 measured reflections

1487 independent reflections
 1305 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 2.6^\circ$
 $h = -9 \rightarrow 9$
 $k = -17 \rightarrow 14$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.081$
 $S = 1.03$
 1487 reflections
 133 parameters
 0 restraints

Hydrogen site location: difference Fourier map
 Only H-atom coordinates refined
 $w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.3165P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.91941 (14)	0.84680 (8)	0.62466 (16)	0.0184 (2)
O1	1.08551 (12)	0.84622 (8)	0.62286 (14)	0.0241 (2)
N2	0.83787 (15)	0.80806 (9)	0.77124 (16)	0.0235 (3)
N3	0.67149 (15)	0.82236 (9)	0.72476 (17)	0.0255 (3)
N4	0.64295 (15)	0.86940 (9)	0.55408 (17)	0.0226 (3)
C5	0.79919 (17)	0.88419 (9)	0.49298 (18)	0.0180 (3)
C6	0.83669 (16)	0.92874 (9)	0.31140 (18)	0.0180 (3)
O7	0.70233 (12)	0.96564 (7)	0.19724 (13)	0.0226 (2)
N8	0.77323 (15)	1.00423 (9)	0.03192 (16)	0.0221 (3)
C9	0.93752 (17)	0.98533 (9)	0.06782 (18)	0.0177 (3)
N10	0.98504 (14)	0.93766 (8)	0.24049 (15)	0.0179 (2)
N1S	0.68154 (15)	1.18606 (9)	0.65235 (17)	0.0205 (3)
H1SA	0.683 (2)	1.1856 (11)	0.789 (3)	0.025*
H1SB	0.782 (2)	1.1628 (12)	0.614 (2)	0.025*
H1SC	0.591 (2)	1.1482 (12)	0.596 (2)	0.025*
N2S	0.65948 (15)	1.28374 (9)	0.57262 (16)	0.0200 (3)
H2SA	0.560 (2)	1.3046 (12)	0.609 (2)	0.024*
H2SB	0.740 (2)	1.3199 (12)	0.636 (2)	0.024*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0201 (5)	0.0188 (6)	0.0166 (5)	-0.0012 (4)	0.0029 (4)	-0.0017 (4)
O1	0.0168 (5)	0.0353 (6)	0.0202 (5)	0.0052 (4)	0.0013 (4)	0.0017 (4)
N2	0.0282 (6)	0.0246 (6)	0.0182 (6)	-0.0028 (5)	0.0046 (5)	0.0026 (5)
N3	0.0232 (6)	0.0308 (7)	0.0230 (6)	-0.0048 (5)	0.0045 (5)	0.0024 (5)
N4	0.0212 (6)	0.0251 (6)	0.0217 (6)	-0.0040 (5)	0.0033 (4)	0.0012 (5)
C5	0.0194 (6)	0.0159 (6)	0.0186 (6)	-0.0012 (5)	0.0014 (5)	-0.0015 (5)
C6	0.0186 (6)	0.0159 (6)	0.0191 (6)	-0.0001 (5)	-0.0007 (5)	-0.0009 (5)
O7	0.0184 (5)	0.0280 (5)	0.0215 (5)	0.0003 (4)	0.0016 (4)	0.0060 (4)
N8	0.0228 (6)	0.0236 (6)	0.0200 (6)	-0.0005 (5)	0.0021 (4)	0.0049 (5)
C9	0.0208 (6)	0.0142 (6)	0.0178 (6)	0.0002 (5)	-0.0001 (5)	0.0005 (5)
N10	0.0196 (5)	0.0169 (5)	0.0172 (5)	0.0004 (4)	0.0016 (4)	0.0014 (4)
N1S	0.0172 (6)	0.0265 (6)	0.0177 (6)	-0.0001 (5)	0.0013 (4)	-0.0002 (5)
N2S	0.0178 (6)	0.0233 (6)	0.0188 (5)	-0.0007 (5)	0.0015 (5)	-0.0025 (5)

Geometric parameters (Å, °)

N1—O1	1.2912 (14)	N8—C9	1.3031 (18)
N1—C5	1.3402 (17)	C9—N10	1.3735 (16)
N1—N2	1.3455 (16)	C9—C9 ⁱ	1.461 (3)
N2—N3	1.3170 (17)	N1S—N2S	1.4476 (16)
N3—N4	1.3373 (17)	N1S—H1SA	0.939 (17)
N4—C5	1.3349 (17)	N1S—H1SB	0.904 (18)
C5—C6	1.4409 (18)	N1S—H1SC	0.930 (18)
C6—N10	1.2968 (17)	N2S—H2SA	0.883 (18)
C6—O7	1.3447 (16)	N2S—H2SB	0.882 (18)
O7—N8	1.4085 (14)		
O1—N1—C5	129.12 (11)	N8—C9—N10	116.02 (12)
O1—N1—N2	122.92 (11)	N8—C9—C9 ⁱ	121.39 (14)
C5—N1—N2	107.96 (11)	N10—C9—C9 ⁱ	122.59 (15)
N3—N2—N1	106.18 (11)	C6—N10—C9	100.99 (11)
N2—N3—N4	111.36 (11)	N2S—N1S—H1SA	112.1 (10)
C5—N4—N3	105.40 (11)	N2S—N1S—H1SB	106.9 (11)
N4—C5—N1	109.11 (11)	H1SA—N1S—H1SB	110.7 (15)
N4—C5—C6	126.67 (12)	N2S—N1S—H1SC	107.3 (10)
N1—C5—C6	124.16 (12)	H1SA—N1S—H1SC	110.6 (14)
N10—C6—O7	114.49 (11)	H1SB—N1S—H1SC	109.1 (14)
N10—C6—C5	128.41 (12)	N1S—N2S—H2SA	105.6 (11)
O7—C6—C5	117.10 (11)	N1S—N2S—H2SB	106.0 (11)
C6—O7—N8	105.70 (10)	H2SA—N2S—H2SB	106.4 (15)
C9—N8—O7	102.79 (10)		
O1—N1—N2—N3	179.57 (11)	N4—C5—C6—O7	5.1 (2)
C5—N1—N2—N3	0.31 (14)	N1—C5—C6—O7	-177.99 (12)
N1—N2—N3—N4	-0.35 (15)	N10—C6—O7—N8	-0.61 (15)
N2—N3—N4—C5	0.26 (15)	C5—C6—O7—N8	179.95 (11)
N3—N4—C5—N1	-0.06 (15)	C6—O7—N8—C9	0.25 (13)
N3—N4—C5—C6	177.23 (13)	O7—N8—C9—N10	0.14 (15)
O1—N1—C5—N4	-179.36 (12)	O7—N8—C9—C9 ⁱ	-179.12 (15)
N2—N1—C5—N4	-0.16 (15)	O7—C6—N10—C9	0.65 (14)
O1—N1—C5—C6	3.3 (2)	C5—C6—N10—C9	-179.98 (13)
N2—N1—C5—C6	-177.52 (12)	N8—C9—N10—C6	-0.48 (15)
N4—C5—C6—N10	-174.25 (13)	C9 ⁱ —C9—N10—C6	178.77 (15)
N1—C5—C6—N10	2.6 (2)		

Symmetry code: (i) $-x+2, -y+2, -z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1S—H1SA...N2S ⁱ	0.939 (17)	2.015 (18)	2.9353 (16)	166.1 (14)
N1S—H1SB...O1 ⁱⁱⁱ	0.904 (18)	2.007 (17)	2.7679 (15)	141.0 (14)
N1S—H1SC...N4 ^{iv}	0.930 (18)	2.018 (18)	2.8778 (17)	153.0 (14)

N2S—H2SA···N3 ^v	0.883 (18)	2.227 (18)	3.0778 (17)	161.6 (15)
N2S—H2SB···O1 ^{vi}	0.882 (18)	2.071 (18)	2.8752 (15)	151.2 (15)

Symmetry codes: (ii) $x, -y+5/2, z+1/2$; (iii) $-x+2, -y+2, -z+1$; (iv) $-x+1, -y+2, -z+1$; (v) $-x+1, y+1/2, -z+3/2$; (vi) $-x+2, y+1/2, -z+3/2$.

Bis(hydroxyammonium) 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1H-tetrazol-1-olate) (2)

Crystal data

$2\text{NH}_4\text{O}^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$

$M_r = 372.26$

Monoclinic, $P2_1/c$

$a = 5.1011$ (9) Å

$b = 18.494$ (3) Å

$c = 7.0044$ (13) Å

$\beta = 92.624$ (2)°

$V = 660.1$ (2) Å³

$Z = 2$

$F(000) = 380$

$D_x = 1.873$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2126 reflections

$\theta = 4.4\text{--}51.8^\circ$

$\mu = 0.17$ mm⁻¹

$T = 296$ K

Plate, colorless

$0.33 \times 0.19 \times 0.02$ mm

Data collection

Bruker SMART APEXII CCD

diffractometer

Radiation source: fine focus sealed tube

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

$T_{\min} = 0.948$, $T_{\max} = 0.997$

5834 measured reflections

1358 independent reflections

1152 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -6 \rightarrow 6$

$k = -23 \rightarrow 23$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.096$

$S = 1.08$

1358 reflections

122 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.1422P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.26439 (19)	0.64777 (6)	0.49548 (14)	0.0199 (3)
N1	0.2362 (2)	0.64703 (6)	0.30834 (18)	0.0170 (3)
N2	0.3978 (2)	0.68219 (7)	0.19563 (19)	0.0208 (3)

N3	0.3121 (3)	0.66943 (7)	0.01809 (19)	0.0227 (3)
N4	0.0995 (2)	0.62648 (7)	0.01466 (18)	0.0204 (3)
C5	0.0547 (3)	0.61257 (8)	0.1968 (2)	0.0168 (3)
C6	-0.1502 (3)	0.56752 (8)	0.2694 (2)	0.0166 (3)
O7	-0.2867 (2)	0.52656 (6)	0.14236 (15)	0.0237 (3)
N8	-0.4729 (3)	0.48950 (7)	0.24763 (19)	0.0234 (3)
C9	-0.4235 (3)	0.51234 (8)	0.4207 (2)	0.0164 (3)
N10	-0.2225 (2)	0.56162 (7)	0.44333 (18)	0.0174 (3)
O1S	-0.1197 (2)	0.72437 (6)	0.61500 (17)	0.0248 (3)
H1S	0.003 (4)	0.6930 (12)	0.578 (3)	0.037*
N1S	-0.2862 (2)	0.68301 (7)	0.72712 (19)	0.0187 (3)
H1SA	-0.392760	0.656491	0.651209	0.028*
H1SB	-0.381130	0.712375	0.797232	0.028*
H1SC	-0.190031	0.654038	0.803773	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0150 (5)	0.0290 (6)	0.0157 (6)	0.0000 (4)	0.0006 (4)	-0.0016 (4)
N1	0.0127 (6)	0.0200 (6)	0.0185 (7)	0.0003 (5)	0.0021 (5)	0.0014 (5)
N2	0.0149 (6)	0.0237 (7)	0.0242 (7)	-0.0007 (5)	0.0056 (5)	0.0018 (5)
N3	0.0181 (6)	0.0263 (7)	0.0241 (7)	0.0005 (5)	0.0056 (5)	0.0034 (5)
N4	0.0168 (6)	0.0243 (7)	0.0205 (7)	0.0009 (5)	0.0040 (5)	0.0027 (5)
C5	0.0128 (6)	0.0198 (7)	0.0178 (8)	0.0022 (5)	0.0003 (5)	0.0005 (5)
C6	0.0135 (7)	0.0182 (7)	0.0180 (8)	0.0013 (5)	-0.0004 (6)	0.0001 (6)
O7	0.0235 (6)	0.0295 (6)	0.0181 (6)	-0.0096 (5)	0.0026 (5)	-0.0011 (4)
N8	0.0219 (7)	0.0272 (7)	0.0213 (7)	-0.0092 (5)	0.0036 (6)	0.0010 (5)
C9	0.0134 (7)	0.0162 (7)	0.0196 (8)	0.0007 (5)	0.0005 (6)	0.0010 (6)
N10	0.0134 (6)	0.0198 (6)	0.0192 (7)	-0.0013 (5)	0.0014 (5)	0.0008 (5)
O1S	0.0181 (5)	0.0238 (6)	0.0335 (7)	-0.0016 (5)	0.0127 (5)	0.0016 (5)
N1S	0.0140 (6)	0.0226 (7)	0.0199 (7)	-0.0015 (5)	0.0032 (5)	0.0008 (5)

Geometric parameters (Å, °)

O1—N1	1.3122 (16)	O7—N8	1.4071 (16)
N1—N2	1.3361 (18)	N8—C9	1.298 (2)
N1—C5	1.3443 (19)	C9—N10	1.3755 (19)
N2—N3	1.3204 (19)	C9—C9 ⁱ	1.459 (3)
N3—N4	1.3436 (18)	O1S—N1S	1.4087 (16)
N4—C5	1.332 (2)	O1S—H1S	0.90 (2)
C5—C6	1.447 (2)	N1S—H1SA	0.8900
C6—N10	1.294 (2)	N1S—H1SB	0.8900
C6—O7	1.3391 (18)	N1S—H1SC	0.8900
O1—N1—N2	122.87 (12)	C9—N8—O7	102.96 (11)
O1—N1—C5	128.79 (12)	N8—C9—N10	115.78 (13)
N2—N1—C5	108.33 (12)	N8—C9—C9 ⁱ	121.42 (17)
N3—N2—N1	106.43 (12)	N10—C9—C9 ⁱ	122.79 (17)

N2—N3—N4	110.78 (12)	C6—N10—C9	100.99 (12)
C5—N4—N3	105.72 (13)	N1S—O1S—H1S	104.8 (13)
N4—C5—N1	108.74 (13)	O1S—N1S—H1SA	109.5
N4—C5—C6	127.32 (13)	O1S—N1S—H1SB	109.5
N1—C5—C6	123.94 (13)	H1SA—N1S—H1SB	109.5
N10—C6—O7	114.58 (13)	O1S—N1S—H1SC	109.5
N10—C6—C5	128.39 (14)	H1SA—N1S—H1SC	109.5
O7—C6—C5	117.03 (13)	H1SB—N1S—H1SC	109.5
C6—O7—N8	105.68 (11)		
O1—N1—N2—N3	179.78 (12)	N4—C5—C6—O7	10.8 (2)
C5—N1—N2—N3	0.58 (15)	N1—C5—C6—O7	-168.32 (13)
N1—N2—N3—N4	-0.30 (15)	N10—C6—O7—N8	0.34 (16)
N2—N3—N4—C5	-0.10 (16)	C5—C6—O7—N8	-179.17 (12)
N3—N4—C5—N1	0.46 (15)	C6—O7—N8—C9	-0.35 (15)
N3—N4—C5—C6	-178.77 (14)	O7—N8—C9—N10	0.29 (17)
O1—N1—C5—N4	-179.80 (13)	O7—N8—C9—C9 ⁱ	179.29 (16)
N2—N1—C5—N4	-0.66 (16)	O7—C6—N10—C9	-0.17 (16)
O1—N1—C5—C6	-0.5 (2)	C5—C6—N10—C9	179.28 (14)
N2—N1—C5—C6	178.61 (13)	N8—C9—N10—C6	-0.09 (17)
N4—C5—C6—N10	-168.63 (15)	C9 ⁱ —C9—N10—C6	-179.08 (17)
N1—C5—C6—N10	12.2 (2)		

Symmetry code: (i) $-x-1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1S—H1S \cdots O1	0.90 (2)	1.70 (2)	2.5880 (15)	169 (2)
N1S—H1SA \cdots O1 ⁱⁱ	0.89	2.02	2.8234 (17)	149
N1S—H1SB \cdots N2 ⁱⁱⁱ	0.89	2.35	2.9713 (19)	127
N1S—H1SC \cdots N4 ^{iv}	0.89	2.10	2.9425 (19)	157

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

Dimethylammonium 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1*H*-tetrazol-1-olate) (3)

Crystal data

$\text{C}_2\text{H}_8\text{N}^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$

$M_r = 396.37$

Triclinic, $P\bar{1}$

$a = 6.0946$ (6) \AA

$b = 8.5197$ (8) \AA

$c = 9.2814$ (9) \AA

$\alpha = 68.259$ (3) $^\circ$

$\beta = 75.957$ (3) $^\circ$

$\gamma = 74.816$ (3) $^\circ$

$V = 426.28$ (7) \AA^3

$Z = 1$

$F(000) = 206$

$D_x = 1.544$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 1925 reflections

$\theta = 4.8\text{--}52.6^\circ$

$\mu = 0.12$ mm^{-1}

$T = 150$ K

Plate, yellow

$0.18 \times 0.12 \times 0.04$ mm

Data collection

Bruker SMART APEXII CCD
diffractometer
Radiation source: fine focus sealed tube
 ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2014)
 $T_{\min} = 0.978$, $T_{\max} = 0.995$
4131 measured reflections

1737 independent reflections
1490 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.4^\circ$
 $h = -7 \rightarrow 7$
 $k = -10 \rightarrow 9$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.04$
1737 reflections
129 parameters
0 restraints

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.1053P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.59547 (17)	0.36241 (13)	0.87451 (12)	0.0211 (2)
N2	0.73348 (18)	0.44045 (14)	0.90588 (12)	0.0246 (3)
N3	0.69908 (19)	0.60180 (14)	0.81186 (13)	0.0259 (3)
N4	0.54333 (18)	0.62953 (14)	0.72093 (12)	0.0241 (2)
C5	0.4791 (2)	0.47875 (15)	0.76160 (14)	0.0205 (3)
C6	0.3133 (2)	0.44918 (15)	0.69185 (14)	0.0201 (3)
O7	0.25452 (15)	0.29342 (11)	0.74431 (10)	0.0248 (2)
N8	0.09343 (19)	0.30587 (14)	0.65217 (13)	0.0249 (3)
C9	0.0765 (2)	0.46521 (15)	0.55884 (13)	0.0201 (3)
N10	0.20941 (17)	0.56041 (13)	0.57819 (11)	0.0210 (2)
O11	0.58447 (16)	0.20008 (11)	0.94750 (10)	0.0258 (2)
N1S	0.26051 (19)	0.04614 (13)	0.19850 (12)	0.0249 (3)
H1SA	0.344680	0.128501	0.137883	0.030*
H1SB	0.312665	-0.045306	0.162814	0.030*
C2S	0.0164 (3)	0.11493 (19)	0.1796 (2)	0.0399 (4)
H2SA	-0.075472	0.026667	0.243664	0.060*
H2SB	0.002362	0.147390	0.068857	0.060*
H2SC	-0.039593	0.216384	0.213810	0.060*

C3S	0.2991 (3)	-0.00899 (18)	0.36271 (16)	0.0326 (3)
H3SA	0.232927	0.086212	0.404837	0.049*
H3SB	0.464886	-0.042153	0.365781	0.049*
H3SC	0.224951	-0.107586	0.426403	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0216 (5)	0.0208 (5)	0.0207 (5)	-0.0039 (4)	-0.0006 (4)	-0.0083 (4)
N2	0.0227 (5)	0.0291 (6)	0.0260 (5)	-0.0061 (4)	-0.0025 (4)	-0.0136 (5)
N3	0.0264 (6)	0.0266 (6)	0.0270 (6)	-0.0078 (4)	-0.0014 (4)	-0.0116 (5)
N4	0.0258 (5)	0.0245 (5)	0.0246 (5)	-0.0083 (4)	-0.0018 (4)	-0.0100 (4)
C5	0.0214 (6)	0.0208 (6)	0.0197 (6)	-0.0042 (5)	-0.0007 (5)	-0.0084 (5)
C6	0.0211 (6)	0.0187 (6)	0.0205 (6)	-0.0047 (5)	0.0013 (5)	-0.0086 (5)
O7	0.0293 (5)	0.0193 (4)	0.0275 (5)	-0.0079 (4)	-0.0099 (4)	-0.0039 (4)
N8	0.0283 (6)	0.0232 (5)	0.0263 (5)	-0.0073 (4)	-0.0093 (4)	-0.0068 (4)
C9	0.0206 (6)	0.0208 (6)	0.0199 (6)	-0.0045 (5)	0.0002 (5)	-0.0096 (5)
N10	0.0224 (5)	0.0199 (5)	0.0219 (5)	-0.0056 (4)	-0.0027 (4)	-0.0077 (4)
O11	0.0326 (5)	0.0183 (4)	0.0250 (5)	-0.0044 (4)	-0.0041 (4)	-0.0061 (3)
N1S	0.0301 (6)	0.0178 (5)	0.0254 (5)	-0.0062 (4)	-0.0009 (4)	-0.0068 (4)
C2S	0.0344 (8)	0.0275 (7)	0.0587 (10)	-0.0035 (6)	-0.0172 (7)	-0.0110 (7)
C3S	0.0452 (8)	0.0251 (7)	0.0269 (7)	-0.0057 (6)	-0.0071 (6)	-0.0077 (5)

Geometric parameters (Å, °)

N1—O11	1.3071 (13)	C9—C9 ⁱ	1.463 (2)
N1—N2	1.3377 (15)	N1S—C2S	1.4767 (18)
N1—C5	1.3440 (16)	N1S—C3S	1.4780 (17)
N2—N3	1.3207 (15)	N1S—H1SA	0.9100
N3—N4	1.3390 (16)	N1S—H1SB	0.9100
N4—C5	1.3334 (16)	C2S—H2SA	0.9800
C5—C6	1.4410 (18)	C2S—H2SB	0.9800
C6—N10	1.2964 (16)	C2S—H2SC	0.9800
C6—O7	1.3460 (14)	C3S—H3SA	0.9800
O7—N8	1.4115 (14)	C3S—H3SB	0.9800
N8—C9	1.3049 (16)	C3S—H3SC	0.9800
C9—N10	1.3671 (16)		
O11—N1—N2	122.67 (10)	C2S—N1S—C3S	113.54 (12)
O11—N1—C5	129.09 (11)	C2S—N1S—H1SA	108.9
N2—N1—C5	108.24 (10)	C3S—N1S—H1SA	108.9
N3—N2—N1	106.11 (10)	C2S—N1S—H1SB	108.9
N2—N3—N4	111.33 (10)	C3S—N1S—H1SB	108.9
C5—N4—N3	105.34 (10)	H1SA—N1S—H1SB	107.7
N4—C5—N1	108.98 (11)	N1S—C2S—H2SA	109.5
N4—C5—C6	124.29 (11)	N1S—C2S—H2SB	109.5
N1—C5—C6	126.73 (12)	H2SA—C2S—H2SB	109.5
N10—C6—O7	113.91 (11)	N1S—C2S—H2SC	109.5

N10—C6—C5	126.23 (11)	H2SA—C2S—H2SC	109.5
O7—C6—C5	119.86 (11)	H2SB—C2S—H2SC	109.5
C6—O7—N8	105.99 (9)	N1S—C3S—H3SA	109.5
C9—N8—O7	102.47 (10)	N1S—C3S—H3SB	109.5
N8—C9—N10	116.05 (11)	H3SA—C3S—H3SB	109.5
N8—C9—C9 ⁱ	121.02 (14)	N1S—C3S—H3SC	109.5
N10—C9—C9 ⁱ	122.94 (13)	H3SA—C3S—H3SC	109.5
C6—N10—C9	101.58 (10)	H3SB—C3S—H3SC	109.5
O11—N1—N2—N3	-179.65 (9)	N4—C5—C6—O7	-177.99 (10)
C5—N1—N2—N3	-0.10 (13)	N1—C5—C6—O7	2.86 (18)
N1—N2—N3—N4	-0.09 (13)	N10—C6—O7—N8	0.34 (13)
N2—N3—N4—C5	0.25 (13)	C5—C6—O7—N8	-179.34 (10)
N3—N4—C5—N1	-0.31 (13)	C6—O7—N8—C9	-0.33 (12)
N3—N4—C5—C6	-179.59 (11)	O7—N8—C9—N10	0.24 (13)
O11—N1—C5—N4	179.77 (10)	O7—N8—C9—C9 ⁱ	-179.89 (13)
N2—N1—C5—N4	0.26 (13)	O7—C6—N10—C9	-0.18 (13)
O11—N1—C5—C6	-1.0 (2)	C5—C6—N10—C9	179.47 (11)
N2—N1—C5—C6	179.52 (11)	N8—C9—N10—C6	-0.05 (14)
N4—C5—C6—N10	2.38 (19)	C9 ⁱ —C9—N10—C6	-179.91 (14)
N1—C5—C6—N10	-176.77 (11)		

Symmetry code: (i) $-x, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1S—H1SA \cdots O11 ⁱⁱ	0.91	2.01	2.8118 (14)	146
N1S—H1SB \cdots O11 ⁱⁱⁱ	0.91	1.85	2.7524 (14)	169

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

Bis(5-amino-1H-tetrazol-4-ium) 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diy)bis(1H-tetrazol-1-olate) (4)

Crystal data

$2\text{CH}_4\text{N}_5^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}\cdot 4\text{H}_2\text{O}$

$M_r = 548.36$

Monoclinic, $P2_1/c$

$a = 24.783$ (2) \AA

$b = 12.7081$ (11) \AA

$c = 6.8396$ (6) \AA

$\beta = 96.289$ (1) $^\circ$

$V = 2141.1$ (3) \AA^3

$Z = 4$

$F(000) = 1128$

$D_x = 1.701$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 5868 reflections

$\theta = 5.9\text{--}52.2^\circ$

$\mu = 0.15$ mm^{-1}

$T = 150$ K

Rod, colorless

$0.28 \times 0.04 \times 0.04$ mm

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: fine focus sealed tube

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2014)

$T_{\min} = 0.960$, $T_{\max} = 0.994$

18508 measured reflections

4274 independent reflections

3489 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 26.2^\circ$, $\theta_{\min} = 0.8^\circ$

$h = -30 \rightarrow 29$
 $k = -15 \rightarrow 15$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.126$
 $S = 1.14$
 4274 reflections
 367 parameters
 0 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0807P)^2 + 0.1085P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.41199 (5)	0.76890 (10)	0.63477 (19)	0.0175 (3)
N2	0.46216 (6)	0.76711 (11)	0.7314 (2)	0.0222 (3)
N3	0.47698 (6)	0.66717 (11)	0.7465 (2)	0.0245 (3)
N4	0.43777 (6)	0.60492 (11)	0.6622 (2)	0.0223 (3)
C5	0.39732 (6)	0.66827 (12)	0.5933 (2)	0.0170 (3)
C6	0.34669 (6)	0.63795 (12)	0.4870 (2)	0.0163 (3)
O7	0.33906 (4)	0.53484 (8)	0.44763 (16)	0.0201 (3)
N8	0.28771 (6)	0.52728 (10)	0.3395 (2)	0.0207 (3)
C9	0.27141 (6)	0.62482 (12)	0.3281 (2)	0.0175 (3)
N10	0.30649 (5)	0.69743 (10)	0.41848 (19)	0.0176 (3)
C11	0.21877 (6)	0.65335 (12)	0.2242 (2)	0.0169 (3)
N12	0.20196 (6)	0.75103 (11)	0.2139 (2)	0.0210 (3)
O13	0.15057 (4)	0.74291 (8)	0.10499 (17)	0.0205 (3)
C14	0.14345 (6)	0.63995 (12)	0.0628 (2)	0.0170 (3)
N15	0.18379 (5)	0.58086 (10)	0.1320 (2)	0.0188 (3)
C16	0.09360 (6)	0.60847 (12)	-0.0484 (2)	0.0176 (3)
N17	0.07914 (5)	0.50775 (10)	-0.08548 (19)	0.0184 (3)
N18	0.02984 (6)	0.50893 (11)	-0.1896 (2)	0.0234 (3)
N19	0.01537 (6)	0.60884 (11)	-0.2111 (2)	0.0233 (3)
N20	0.05393 (5)	0.67176 (11)	-0.1253 (2)	0.0214 (3)
O21	0.38511 (5)	0.85499 (9)	0.59296 (17)	0.0235 (3)
O22	0.10524 (5)	0.42236 (9)	-0.03543 (19)	0.0280 (3)
C23	-0.12543 (7)	0.63807 (13)	-0.5210 (2)	0.0197 (4)
N24	-0.12672 (6)	0.53320 (10)	-0.5150 (2)	0.0215 (3)

H24	-0.100593	0.492838	-0.459091	0.026*
N25	-0.17470 (6)	0.49815 (12)	-0.6087 (2)	0.0283 (4)
N26	-0.20249 (6)	0.57784 (11)	-0.6713 (2)	0.0287 (4)
N27	-0.17293 (6)	0.66536 (11)	-0.6197 (2)	0.0223 (3)
H27	-0.183456	0.730349	-0.647016	0.027*
N28	-0.08567 (6)	0.70014 (11)	-0.4466 (2)	0.0270 (4)
H28A	-0.055908	0.672818	-0.384994	0.032*
H28B	-0.088925	0.768859	-0.458745	0.032*
C29	0.62509 (7)	0.63910 (13)	0.9981 (2)	0.0208 (4)
N30	0.62287 (6)	0.74382 (11)	1.0154 (2)	0.0234 (3)
H30	0.594969	0.783225	0.971237	0.028*
N31	0.67036 (6)	0.78048 (12)	1.1116 (2)	0.0269 (4)
N32	0.70102 (6)	0.70206 (12)	1.1553 (2)	0.0277 (4)
N33	0.67412 (6)	0.61364 (11)	1.0874 (2)	0.0237 (3)
H33	0.687071	0.549235	1.100304	0.028*
N34	0.58793 (6)	0.57604 (11)	0.9108 (2)	0.0272 (4)
H34A	0.557155	0.602056	0.854686	0.033*
H34B	0.593824	0.507786	0.908483	0.033*
O1S	-0.05800 (5)	0.39192 (10)	-0.35612 (19)	0.0270 (3)
H1SA	-0.0549 (9)	0.328 (2)	-0.374 (3)	0.041*
H1SB	-0.0263 (9)	0.4142 (18)	-0.305 (3)	0.041*
O2S	0.71190 (6)	0.42019 (10)	1.1563 (2)	0.0282 (3)
H2SA	0.7426 (10)	0.4009 (18)	1.192 (3)	0.042*
H2SB	0.6979 (10)	0.3689 (19)	1.103 (3)	0.042*
O3S	-0.20626 (6)	0.85908 (10)	-0.6897 (2)	0.0330 (3)
H3SA	-0.2354 (11)	0.8812 (19)	-0.736 (4)	0.049*
H3SB	-0.1880 (11)	0.907 (2)	-0.639 (4)	0.049*
O4S	0.44686 (6)	0.38490 (11)	0.6275 (3)	0.0438 (4)
H4SA	0.4454 (11)	0.447 (3)	0.636 (4)	0.066*
H4SB	0.4770 (11)	0.367 (2)	0.674 (4)	0.066*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0158 (7)	0.0142 (7)	0.0216 (7)	-0.0010 (5)	-0.0014 (5)	-0.0011 (5)
N2	0.0164 (7)	0.0201 (7)	0.0285 (7)	-0.0001 (6)	-0.0053 (6)	-0.0022 (6)
N3	0.0177 (7)	0.0202 (7)	0.0334 (8)	0.0007 (6)	-0.0069 (6)	-0.0038 (6)
N4	0.0177 (7)	0.0178 (7)	0.0299 (7)	0.0011 (5)	-0.0046 (6)	-0.0017 (6)
C5	0.0150 (8)	0.0144 (8)	0.0210 (8)	-0.0006 (6)	-0.0007 (6)	-0.0003 (6)
C6	0.0153 (8)	0.0122 (7)	0.0212 (8)	-0.0018 (6)	0.0005 (6)	-0.0008 (6)
O7	0.0158 (6)	0.0127 (6)	0.0302 (6)	0.0000 (4)	-0.0054 (5)	-0.0008 (5)
N8	0.0148 (7)	0.0147 (7)	0.0306 (7)	-0.0013 (5)	-0.0072 (6)	-0.0014 (5)
C9	0.0147 (8)	0.0141 (8)	0.0229 (8)	-0.0020 (6)	-0.0017 (6)	-0.0006 (6)
N10	0.0146 (7)	0.0140 (7)	0.0235 (7)	-0.0012 (5)	-0.0019 (5)	-0.0007 (5)
C11	0.0142 (8)	0.0145 (8)	0.0212 (8)	-0.0016 (6)	-0.0012 (6)	-0.0003 (6)
N12	0.0146 (7)	0.0169 (7)	0.0295 (7)	-0.0011 (5)	-0.0077 (6)	-0.0003 (6)
O13	0.0155 (6)	0.0129 (6)	0.0309 (6)	0.0005 (4)	-0.0070 (5)	-0.0029 (5)
C14	0.0160 (8)	0.0123 (7)	0.0222 (8)	-0.0013 (6)	-0.0004 (6)	-0.0006 (6)

N15	0.0159 (7)	0.0130 (7)	0.0264 (7)	-0.0013 (5)	-0.0031 (6)	-0.0008 (5)
C16	0.0155 (8)	0.0121 (7)	0.0245 (8)	-0.0008 (6)	-0.0014 (7)	0.0001 (6)
N17	0.0140 (7)	0.0130 (7)	0.0268 (7)	-0.0002 (5)	-0.0039 (6)	-0.0004 (5)
N18	0.0166 (7)	0.0187 (7)	0.0326 (8)	-0.0010 (6)	-0.0073 (6)	-0.0005 (6)
N19	0.0177 (7)	0.0192 (7)	0.0310 (8)	-0.0008 (6)	-0.0059 (6)	0.0011 (6)
N20	0.0163 (7)	0.0174 (7)	0.0288 (7)	0.0004 (5)	-0.0046 (6)	0.0002 (6)
O21	0.0212 (6)	0.0127 (6)	0.0350 (7)	0.0028 (5)	-0.0046 (5)	0.0003 (5)
O22	0.0229 (7)	0.0109 (6)	0.0471 (8)	0.0019 (5)	-0.0096 (6)	0.0012 (5)
C23	0.0210 (8)	0.0161 (8)	0.0213 (8)	0.0023 (7)	-0.0008 (7)	0.0010 (6)
N24	0.0200 (7)	0.0132 (7)	0.0298 (7)	0.0014 (6)	-0.0043 (6)	0.0018 (6)
N25	0.0233 (8)	0.0194 (8)	0.0402 (8)	-0.0015 (6)	-0.0066 (7)	0.0003 (6)
N26	0.0257 (9)	0.0171 (7)	0.0408 (9)	-0.0009 (6)	-0.0072 (7)	0.0008 (6)
N27	0.0208 (8)	0.0141 (7)	0.0304 (7)	0.0015 (6)	-0.0042 (6)	0.0005 (6)
N28	0.0241 (8)	0.0137 (7)	0.0400 (8)	0.0011 (6)	-0.0104 (7)	0.0025 (6)
C29	0.0214 (9)	0.0175 (8)	0.0231 (8)	0.0032 (7)	0.0008 (7)	0.0005 (6)
N30	0.0214 (8)	0.0164 (7)	0.0311 (8)	0.0027 (6)	-0.0034 (6)	-0.0004 (6)
N31	0.0242 (8)	0.0209 (8)	0.0341 (8)	-0.0001 (6)	-0.0039 (6)	-0.0025 (6)
N32	0.0254 (8)	0.0199 (8)	0.0360 (8)	-0.0010 (6)	-0.0050 (6)	-0.0032 (6)
N33	0.0233 (8)	0.0145 (7)	0.0320 (8)	0.0033 (6)	-0.0033 (6)	-0.0006 (6)
N34	0.0252 (8)	0.0143 (7)	0.0396 (9)	0.0031 (6)	-0.0075 (7)	-0.0013 (6)
O1S	0.0226 (7)	0.0135 (6)	0.0419 (8)	-0.0003 (5)	-0.0104 (6)	-0.0006 (5)
O2S	0.0251 (7)	0.0140 (6)	0.0428 (8)	0.0003 (5)	-0.0089 (6)	-0.0010 (5)
O3S	0.0287 (8)	0.0135 (6)	0.0527 (9)	0.0011 (5)	-0.0136 (6)	-0.0011 (6)
O4S	0.0241 (8)	0.0160 (7)	0.0854 (12)	0.0032 (6)	-0.0204 (8)	-0.0083 (7)

Geometric parameters (Å, °)

N1—O21	1.2964 (17)	C23—N27	1.337 (2)
N1—N2	1.3429 (19)	N24—N25	1.362 (2)
N1—C5	1.351 (2)	N24—H24	0.8800
N2—N3	1.3230 (19)	N25—N26	1.272 (2)
N3—N4	1.3342 (19)	N26—N27	1.357 (2)
N4—C5	1.331 (2)	N27—H27	0.8800
C5—C6	1.432 (2)	N28—H28A	0.8800
C6—N10	1.297 (2)	N28—H28B	0.8800
C6—O7	1.3468 (18)	C29—N34	1.314 (2)
O7—N8	1.4033 (16)	C29—N30	1.338 (2)
N8—C9	1.303 (2)	C29—N33	1.338 (2)
C9—N10	1.368 (2)	N30—N31	1.366 (2)
C9—C11	1.461 (2)	N30—H30	0.8800
C11—N12	1.309 (2)	N31—N32	1.269 (2)
C11—N15	1.3704 (19)	N32—N33	1.362 (2)
N12—O13	1.4071 (17)	N33—H33	0.8800
O13—C14	1.3473 (18)	N34—H34A	0.8800
C14—N15	1.298 (2)	N34—H34B	0.8800
C14—C16	1.435 (2)	O1S—H1SA	0.83 (3)
C16—N20	1.333 (2)	O1S—H1SB	0.87 (2)
C16—N17	1.346 (2)	O2S—H2SA	0.81 (2)

N17—O22	1.2902 (17)	O2S—H2SB	0.81 (3)
N17—N18	1.3450 (19)	O3S—H3SA	0.81 (2)
N18—N19	1.3232 (19)	O3S—H3SB	0.82 (3)
N19—N20	1.3322 (19)	O4S—H4SA	0.79 (3)
C23—N28	1.320 (2)	O4S—H4SB	0.81 (3)
C23—N24	1.334 (2)		
O21—N1—N2	123.26 (12)	N18—N19—N20	110.74 (13)
O21—N1—C5	129.24 (13)	N19—N20—C16	105.92 (13)
N2—N1—C5	107.49 (12)	N28—C23—N24	127.21 (15)
N3—N2—N1	106.79 (12)	N28—C23—N27	128.20 (15)
N2—N3—N4	110.65 (13)	N24—C23—N27	104.59 (14)
C5—N4—N3	106.20 (13)	C23—N24—N25	109.56 (13)
N4—C5—N1	108.87 (14)	C23—N24—H24	125.2
N4—C5—C6	126.93 (14)	N25—N24—H24	125.2
N1—C5—C6	124.17 (14)	N26—N25—N24	108.08 (14)
N10—C6—O7	114.16 (13)	N25—N26—N27	107.94 (14)
N10—C6—C5	128.49 (14)	C23—N27—N26	109.82 (14)
O7—C6—C5	117.34 (13)	C23—N27—H27	125.1
C6—O7—N8	105.75 (11)	N26—N27—H27	125.1
C9—N8—O7	102.93 (12)	C23—N28—H28A	120.0
N8—C9—N10	115.91 (14)	C23—N28—H28B	120.0
N8—C9—C11	121.30 (14)	H28A—N28—H28B	120.0
N10—C9—C11	122.79 (14)	N34—C29—N30	127.83 (16)
C6—N10—C9	101.26 (13)	N34—C29—N33	128.02 (15)
N12—C11—N15	115.54 (14)	N30—C29—N33	104.15 (14)
N12—C11—C9	121.58 (14)	C29—N30—N31	109.89 (14)
N15—C11—C9	122.88 (14)	C29—N30—H30	125.1
C11—N12—O13	102.91 (12)	N31—N30—H30	125.1
C14—O13—N12	105.92 (11)	N32—N31—N30	107.93 (14)
N15—C14—O13	113.96 (13)	N31—N32—N33	108.03 (14)
N15—C14—C16	128.05 (14)	C29—N33—N32	110.00 (14)
O13—C14—C16	117.99 (13)	C29—N33—H33	125.0
C14—N15—C11	101.67 (13)	N32—N33—H33	125.0
N20—C16—N17	109.25 (13)	C29—N34—H34A	120.0
N20—C16—C14	126.58 (14)	C29—N34—H34B	120.0
N17—C16—C14	124.14 (14)	H34A—N34—H34B	120.0
O22—N17—N18	123.35 (13)	H1SA—O1S—H1SB	106 (2)
O22—N17—C16	129.37 (13)	H2SA—O2S—H2SB	104 (2)
N18—N17—C16	107.28 (12)	H3SA—O3S—H3SB	110 (2)
N19—N18—N17	106.80 (12)	H4SA—O4S—H4SB	107 (3)
O21—N1—N2—N3	-179.48 (14)	O13—C14—N15—C11	-0.16 (18)
C5—N1—N2—N3	0.14 (17)	C16—C14—N15—C11	-179.50 (16)
N1—N2—N3—N4	0.05 (19)	N12—C11—N15—C14	-0.14 (19)
N2—N3—N4—C5	-0.22 (19)	C9—C11—N15—C14	179.76 (15)
N3—N4—C5—N1	0.30 (18)	N15—C14—C16—N20	-176.68 (16)
N3—N4—C5—C6	178.57 (15)	O13—C14—C16—N20	4.0 (2)

O21—N1—C5—N4	179.30 (15)	N15—C14—C16—N17	5.5 (3)
N2—N1—C5—N4	-0.28 (18)	O13—C14—C16—N17	-173.77 (15)
O21—N1—C5—C6	1.0 (3)	N20—C16—N17—O22	-179.06 (15)
N2—N1—C5—C6	-178.60 (14)	C14—C16—N17—O22	-0.9 (3)
N4—C5—C6—N10	179.82 (16)	N20—C16—N17—N18	0.78 (18)
N1—C5—C6—N10	-2.2 (3)	C14—C16—N17—N18	178.89 (15)
N4—C5—C6—O7	-1.6 (2)	O22—N17—N18—N19	179.15 (14)
N1—C5—C6—O7	176.45 (14)	C16—N17—N18—N19	-0.70 (18)
N10—C6—O7—N8	0.35 (18)	N17—N18—N19—N20	0.38 (18)
C5—C6—O7—N8	-178.46 (13)	N18—N19—N20—C16	0.10 (18)
C6—O7—N8—C9	-0.01 (16)	N17—C16—N20—N19	-0.54 (18)
O7—N8—C9—N10	-0.31 (18)	C14—C16—N20—N19	-178.59 (15)
O7—N8—C9—C11	179.62 (14)	N28—C23—N24—N25	-179.78 (17)
O7—C6—N10—C9	-0.50 (18)	N27—C23—N24—N25	-0.22 (18)
C5—C6—N10—C9	178.15 (16)	C23—N24—N25—N26	0.0 (2)
N8—C9—N10—C6	0.51 (19)	N24—N25—N26—N27	0.2 (2)
C11—C9—N10—C6	-179.43 (15)	N28—C23—N27—N26	179.88 (17)
N8—C9—C11—N12	179.34 (16)	N24—C23—N27—N26	0.33 (18)
N10—C9—C11—N12	-0.7 (2)	N25—N26—N27—C23	-0.3 (2)
N8—C9—C11—N15	-0.6 (2)	N34—C29—N30—N31	-178.26 (17)
N10—C9—C11—N15	179.38 (15)	N33—C29—N30—N31	0.79 (18)
N15—C11—N12—O13	0.36 (18)	C29—N30—N31—N32	-0.74 (19)
C9—C11—N12—O13	-179.54 (14)	N30—N31—N32—N33	0.35 (19)
C11—N12—O13—C14	-0.42 (16)	N34—C29—N33—N32	178.47 (17)
N12—O13—C14—N15	0.38 (18)	N30—C29—N33—N32	-0.58 (19)
N12—O13—C14—C16	179.79 (13)	N31—N32—N33—C29	0.1 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N24—H24 \cdots O1S	0.88	1.76	2.6267 (18)	169
N27—H27 \cdots O3S	0.88	1.74	2.6241 (19)	177
N28—H28A \cdots N19	0.88	2.18	3.054 (2)	176
N28—H28B \cdots O22 ⁱ	0.88	1.99	2.8656 (19)	172
N30—H30 \cdots O4S ⁱⁱ	0.88	1.75	2.605 (2)	165
N33—H33 \cdots O2S	0.88	1.78	2.6544 (19)	173
N34—H34A \cdots N3	0.88	2.20	3.080 (2)	174
N34—H34B \cdots O21 ⁱⁱⁱ	0.88	2.01	2.8882 (19)	175
O1S—H1SA \cdots N20 ^{iv}	0.83 (3)	1.99 (3)	2.8030 (19)	170 (2)
O1S—H1SB \cdots N18	0.87 (2)	1.94 (2)	2.7758 (19)	160 (2)
O2S—H2SA \cdots N12 ⁱⁱⁱ	0.81 (2)	2.39 (2)	3.0906 (18)	144 (2)
O2S—H2SB \cdots N10 ⁱⁱⁱ	0.81 (3)	2.19 (2)	2.9038 (18)	148 (2)
O3S—H3SA \cdots N8 ⁱ	0.81 (2)	2.33 (2)	3.0397 (19)	147 (2)
O3S—H3SB \cdots N15 ⁱ	0.82 (3)	2.21 (3)	2.8915 (19)	141 (2)
O4S—H4SA \cdots N4	0.79 (3)	2.03 (3)	2.817 (2)	177 (3)
O4S—H4SB \cdots N2 ⁱⁱⁱ	0.81 (3)	2.02 (3)	2.789 (2)	157 (3)

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

Bis(aminoguanidinium) 5,5'-(3,3'-bi[1,2,4-oxadiazole]-5,5'-diyl)bis(1H-tetrazol-1-olate) (5)*Crystal data* $2\text{C}_7\text{H}_7\text{N}_4^+\cdot\text{C}_6\text{N}_{12}\text{O}_4^{2-}$ $M_r = 454.39$ Monoclinic, $P2_1/n$ $a = 7.9458$ (4) Å $b = 5.5586$ (2) Å $c = 20.6066$ (9) Å $\beta = 97.647$ (2)° $V = 902.05$ (7) Å³ $Z = 2$ $F(000) = 468$ $D_x = 1.673$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4111 reflections

 $\theta = 2.9$ – 26.4 ° $\mu = 0.14$ mm⁻¹ $T = 150$ K

Rod, yellow

 $0.42 \times 0.11 \times 0.08$ mm*Data collection*

Bruker SMART APEXII CCD

diffractometer

Radiation source: fine focus sealed tube

 ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

 $T_{\min} = 0.944$, $T_{\max} = 0.989$

7786 measured reflections

1844 independent reflections

1633 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.020$ $\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.7$ ° $h = -9 \rightarrow 9$ $k = -6 \rightarrow 6$ $l = -25 \rightarrow 25$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.134$ $S = 1.06$

1844 reflections

206 parameters

63 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.8763P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.74$ e Å⁻³ $\Delta\rho_{\min} = -0.24$ e Å⁻³*Special details*

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1A	0.7242 (6)	0.6920 (8)	0.89476 (16)	0.0200 (8)	0.907 (5)
N2A	0.7542 (4)	0.8420 (6)	0.84668 (15)	0.0249 (7)	0.907 (5)
N3A	0.6683 (3)	0.7570 (6)	0.79207 (13)	0.0273 (7)	0.907 (5)
N4A	0.5827 (5)	0.5580 (6)	0.80370 (19)	0.0256 (8)	0.907 (5)
C5A	0.6185 (8)	0.5198 (9)	0.8676 (2)	0.0197 (10)	0.907 (5)
O11A	0.7863 (2)	0.7262 (3)	0.95566 (8)	0.0277 (5)	0.907 (5)
N1B	0.599 (6)	0.619 (7)	0.809 (2)	0.025 (7)	0.093 (5)

N2B	0.685 (4)	0.813 (5)	0.8096 (18)	0.019 (5)	0.093 (5)
N3B	0.774 (5)	0.878 (6)	0.8619 (17)	0.021 (5)	0.093 (5)
N4B	0.744 (6)	0.696 (10)	0.909 (2)	0.020 (6)	0.093 (5)
C5B	0.635 (10)	0.536 (10)	0.878 (3)	0.023 (8)	0.093 (5)
O11B	0.483 (2)	0.528 (3)	0.7672 (8)	0.030 (5)	0.093 (5)
C6	0.5571 (2)	0.3235 (3)	0.90328 (9)	0.0191 (4)	
O7	0.44405 (17)	0.1736 (2)	0.86989 (6)	0.0226 (3)	
N8	0.4063 (2)	-0.0012 (3)	0.91550 (8)	0.0222 (4)	
C9	0.5000 (2)	0.0668 (3)	0.96935 (8)	0.0192 (4)	
N10	0.5969 (2)	0.2681 (3)	0.96468 (7)	0.0203 (4)	
N12	0.1089 (3)	0.6386 (5)	0.79393 (10)	0.0481 (6)	
H12A	0.167 (3)	0.578 (5)	0.7645 (10)	0.058*	
H12B	0.029 (3)	0.723 (5)	0.7706 (13)	0.058*	
N13	0.0329 (3)	0.4421 (4)	0.82311 (9)	0.0403 (5)	
H13	-0.0403	0.3478	0.7995	0.048*	
C14	0.0749 (2)	0.4033 (4)	0.88724 (10)	0.0276 (5)	
N15	0.0053 (3)	0.2218 (4)	0.91527 (10)	0.0387 (5)	
H15A	0.0311	0.1965	0.9576	0.046*	
H15B	-0.0670	0.1262	0.8917	0.046*	
N16	0.1827 (2)	0.5488 (3)	0.92093 (8)	0.0296 (4)	
H16A	0.2103	0.5268	0.9633	0.036*	
H16B	0.2276	0.6687	0.9012	0.036*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1A	0.0220 (15)	0.0203 (11)	0.0168 (18)	0.0009 (10)	-0.0010 (12)	-0.0005 (13)
N2A	0.0294 (15)	0.0221 (14)	0.0221 (17)	-0.0029 (10)	-0.0001 (14)	0.0003 (11)
N3A	0.0349 (14)	0.0276 (14)	0.0182 (13)	-0.0039 (10)	-0.0012 (10)	0.0013 (10)
N4A	0.0295 (18)	0.0255 (17)	0.0210 (13)	-0.0052 (12)	0.0004 (11)	0.0027 (12)
C5A	0.019 (2)	0.0215 (13)	0.018 (2)	-0.0001 (11)	0.0004 (15)	-0.0022 (12)
O11A	0.0332 (9)	0.0290 (9)	0.0185 (10)	-0.0056 (7)	-0.0054 (7)	-0.0019 (6)
N1B	0.030 (11)	0.023 (9)	0.019 (7)	-0.006 (8)	-0.006 (6)	0.008 (5)
N2B	0.021 (6)	0.019 (6)	0.017 (6)	-0.002 (3)	0.004 (3)	0.003 (3)
N3B	0.022 (6)	0.021 (6)	0.021 (6)	0.001 (3)	0.001 (3)	0.001 (3)
N4B	0.020 (11)	0.022 (8)	0.017 (8)	-0.006 (7)	-0.002 (6)	0.005 (6)
C5B	0.026 (14)	0.027 (9)	0.013 (8)	-0.005 (10)	-0.004 (7)	0.007 (6)
O11B	0.032 (7)	0.036 (8)	0.020 (7)	-0.008 (6)	-0.001 (6)	0.002 (5)
C6	0.0170 (8)	0.0210 (9)	0.0186 (8)	0.0006 (7)	0.0000 (6)	-0.0025 (7)
O7	0.0251 (7)	0.0244 (7)	0.0172 (6)	-0.0043 (6)	-0.0015 (5)	-0.0004 (5)
N8	0.0256 (8)	0.0233 (8)	0.0173 (7)	-0.0040 (6)	0.0010 (6)	0.0001 (6)
C9	0.0196 (8)	0.0203 (9)	0.0174 (9)	-0.0008 (7)	0.0015 (6)	-0.0019 (7)
N10	0.0217 (8)	0.0215 (8)	0.0174 (8)	-0.0020 (6)	0.0008 (6)	-0.0009 (6)
N12	0.0518 (13)	0.0630 (16)	0.0285 (10)	0.0028 (12)	0.0017 (9)	0.0059 (10)
N13	0.0441 (11)	0.0451 (12)	0.0282 (10)	-0.0039 (9)	-0.0081 (8)	-0.0064 (9)
C14	0.0225 (9)	0.0272 (11)	0.0319 (11)	0.0016 (8)	-0.0007 (8)	-0.0078 (9)
N15	0.0361 (10)	0.0349 (11)	0.0430 (11)	-0.0086 (8)	-0.0031 (9)	-0.0020 (9)
N16	0.0304 (9)	0.0324 (10)	0.0241 (8)	-0.0078 (8)	-0.0037 (7)	-0.0027 (7)

Geometric parameters (Å, °)

N1A—O11A	1.300 (3)	O7—N8	1.411 (2)
N1A—N2A	1.341 (5)	N8—C9	1.307 (2)
N1A—C5A	1.345 (5)	C9—N10	1.369 (2)
N2A—N3A	1.323 (3)	C9—C9 ⁱ	1.465 (4)
N3A—N4A	1.337 (4)	N12—N13	1.420 (3)
N4A—C5A	1.328 (5)	N12—H12A	0.8800 (11)
C5A—C6	1.436 (4)	N12—H12B	0.8801 (11)
N1B—N2B	1.28 (5)	N13—C14	1.337 (3)
N1B—O11B	1.28 (4)	N13—H13	0.8800
N1B—C5B	1.48 (7)	C14—N16	1.309 (3)
N2B—N3B	1.26 (4)	C14—N15	1.320 (3)
N3B—N4B	1.45 (6)	N15—H15A	0.8800
N4B—C5B	1.34 (7)	N15—H15B	0.8800
C5B—C6	1.46 (2)	N16—H16A	0.8800
C6—N10	1.300 (2)	N16—H16B	0.8800
C6—O7	1.345 (2)		
O11A—N1A—N2A	122.7 (4)	O7—C6—C5B	127 (2)
O11A—N1A—C5A	129.9 (4)	C6—O7—N8	105.81 (13)
N2A—N1A—C5A	107.4 (3)	C9—N8—O7	102.65 (14)
N3A—N2A—N1A	106.5 (3)	N8—C9—N10	116.01 (16)
N2A—N3A—N4A	111.1 (3)	N8—C9—C9 ⁱ	121.4 (2)
C5A—N4A—N3A	105.3 (2)	N10—C9—C9 ⁱ	122.6 (2)
N4A—C5A—N1A	109.8 (3)	C6—N10—C9	101.30 (15)
N4A—C5A—C6	125.9 (3)	N13—N12—H12A	107 (2)
N1A—C5A—C6	124.3 (4)	N13—N12—H12B	109 (2)
N2B—N1B—O11B	132 (4)	H12A—N12—H12B	104 (3)
N2B—N1B—C5B	103 (3)	C14—N13—N12	118.59 (19)
O11B—N1B—C5B	124 (4)	C14—N13—H13	120.7
N3B—N2B—N1B	119 (3)	N12—N13—H13	120.7
N2B—N3B—N4B	105 (3)	N16—C14—N15	121.5 (2)
C5B—N4B—N3B	107 (4)	N16—C14—N13	119.0 (2)
N4B—C5B—C6	129 (5)	N15—C14—N13	119.5 (2)
N4B—C5B—N1B	107 (3)	C14—N15—H15A	120.0
C6—C5B—N1B	124 (4)	C14—N15—H15B	120.0
N10—C6—O7	114.22 (17)	H15A—N15—H15B	120.0
N10—C6—C5A	128.5 (2)	C14—N16—H16A	120.0
O7—C6—C5A	117.3 (2)	C14—N16—H16B	120.0
N10—C6—C5B	119 (2)	H16A—N16—H16B	120.0
O11A—N1A—N2A—N3A	−178.2 (4)	N1A—C5A—C6—N10	−4.2 (8)
C5A—N1A—N2A—N3A	−0.6 (5)	N4A—C5A—C6—O7	−4.8 (8)
N1A—N2A—N3A—N4A	0.6 (4)	N1A—C5A—C6—O7	176.2 (5)
N2A—N3A—N4A—C5A	−0.3 (5)	N4B—C5B—C6—N10	−2 (10)
N3A—N4A—C5A—N1A	0.0 (6)	N1B—C5B—C6—N10	−179 (5)
N3A—N4A—C5A—C6	−179.2 (5)	N4B—C5B—C6—O7	177 (6)

O11A—N1A—C5A—N4A	177.8 (5)	N1B—C5B—C6—O7	0 (10)
N2A—N1A—C5A—N4A	0.4 (6)	N10—C6—O7—N8	-0.1 (2)
O11A—N1A—C5A—C6	-3.0 (9)	C5A—C6—O7—N8	179.5 (4)
N2A—N1A—C5A—C6	179.6 (5)	C5B—C6—O7—N8	-180 (5)
O11B—N1B—N2B—N3B	170 (5)	C6—O7—N8—C9	0.14 (18)
C5B—N1B—N2B—N3B	2 (6)	O7—N8—C9—N10	-0.1 (2)
N1B—N2B—N3B—N4B	-2 (5)	O7—N8—C9—C9 ⁱ	179.9 (2)
N2B—N3B—N4B—C5B	1 (6)	O7—C6—N10—C9	0.0 (2)
N3B—N4B—C5B—C6	-177 (7)	C5A—C6—N10—C9	-179.6 (4)
N3B—N4B—C5B—N1B	0 (7)	C5B—C6—N10—C9	180 (4)
N2B—N1B—C5B—N4B	-1 (7)	N8—C9—N10—C6	0.1 (2)
O11B—N1B—C5B—N4B	-170 (5)	C9 ⁱ —C9—N10—C6	-180.0 (2)
N2B—N1B—C5B—C6	176 (6)	N12—N13—C14—N16	0.8 (3)
O11B—N1B—C5B—C6	7 (10)	N12—N13—C14—N15	179.8 (2)
N4A—C5A—C6—N10	174.8 (5)		

Symmetry code: (i) $-x+1, -y, -z+2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N12—H12B \cdots N4A ⁱⁱ	0.88 (1)	2.50 (1)	3.314 (4)	155 (3)
N13—H13 \cdots N3A ⁱⁱⁱ	0.88	2.08	2.870 (3)	149
N13—H13 \cdots N4A ⁱⁱⁱ	0.88	2.65	3.405 (4)	144
N15—H15A \cdots O11A ^{iv}	0.88	2.19	2.954 (3)	145
N15—H15B \cdots N2A ^v	0.88	2.24	3.112 (4)	170
N16—H16A \cdots O11A ^{iv}	0.88	2.18	2.949 (2)	146
N16—H16A \cdots N10 ^{iv}	0.88	2.29	2.926 (2)	129
N16—H16B \cdots N8 ^{vi}	0.88	2.32	3.079 (2)	145

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