Isostructural rubidium and caesium 4-(3,5-dinitropyrazol-4-yl)-3,5-dinitropyrazolates: crystal engineering with polynitro energetic species

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In the structures of the title salts, poly[[µ-4-(3,5-dinitropyrazol-4-yl)-3,5-dinitropyrazol-1-ido]rubidium], [Rb(C₆HN₈O₈)ₙ], (1), and its isostructural caesium analogue [Cs(C₆HN₈O₈)ₙ], (2), two independent cations M₁ and M₂ (M = Rb, Cs) are situated on a crystallographic twofold axis and on a center of inversion, respectively. Mutual intermolecular hydrogen bonding between the conjugate 3,5-dinitopyrazole NH-donor and 3,5-dinitropyrazole N-acceptor sites of the anions [N–N = 2.785 (2) Å for (1) and 2.832 (3) Å for (2)] governs the self-assembly of the translation-related anions in a predictable fashion. Such one-component modular construction of the organic subtopology supports the utility of the crystal-engineering approach towards designing the structures of polynitro energetic materials. The anionic chains are further linked by multiple ion–dipole interactions involving the 12-coordinate cations bonded to two pyrazole N-atoms [Rb–N = 3.1285 (16), 3.2261 (16) Å; Cs–N = 3.369 (2), 3.401 (2) Å] and all of the eight nitro O-atoms [Rb–O = 2.8543 (15)–3.6985 (16) Å; Cs–O = 3.071 (2)–3.811 (2) Å]. The resulting ionic networks follow the CsCl topological archetype, with either metal or organic ions residing in an environment of eight counter-ions. Weak lone pair–π-hole interactions [pyrazole-N atoms to NO₂ groups; N–N = 2.990 (3)–3.198 (3) Å] are also relevant to the packing. The Hirshfeld surfaces and percentage two-dimensional fingerprint plots for (1) and (2) are described.

1. Chemical context

Many issues of crystal engineering, in regard to control over bonding patterns, supramolecular topologies, molecular packing, and crystal morphologies are highly relevant to the area of energetic materials. In particular, non-covalent contacts involving common explosophile nitro groups (Bauzá et al., 2017) establish pathways to transmit intermolecular interactions and they are often responsible for higher densities of the solids (Zhang et al., 2000). The layered architectures of the energetic solids provide better buffering against external mechanical stimuli, which is essential for developing insensitive materials (Zhang et al., 2008). At the same time, incorporation of specific coordination geometries for the assembly of metal–organic solids offers potential for the synthesis of new perchlorate-free flame colorants and pyrotechnics (Glück et al., 2017). However, successful applications of the crystal-engineering methodology toward designing the structures of polynitro compounds are relatively rare, so far (Domasevitch et al., 2020). This is predetermined by a lack of reliable supramolecular synthons comprising the nitro groups, which are only weak acceptors of conventional hydrogen...
bonds (Robinson et al., 2000) and are only weak donors with respect to the metal ions. A more severe limitation is associated with the need for direct bonding between the nitro-rich functionalities only, since the incorporation of any low-energetic component or solvent molecules is an inevitable penalty to the performance. Such dilution of the energetic moieties in the crystals is relevant, for example, to a series of hydrogen-bonded solids prepared by Aakerøy et al. (2015) with acidic ethylenedinitramine and common bitopic pyridine-N bases.

Recently, we have reported a new strategy for the construction of energetic salts, which offers higher degree of control over the structure. Double functionality of the well-performing material 3,3′,5,5′-tetranitro-4,4′-bipyrazole [H₃(TNBP)] (Domasevitch et al., 2019) grants synthetic access either to singly or doubly anionic species [H(TNBP)]⁻ and [TNBP]²⁻, respectively. The former combine conjugate nitropyrazole donor and dinitropyrazolate acceptor sites for sustaining particularly strong N−H⋯N bonding. In fact, such bonding of two explosophores dominated the self-assembly in a very predictable fashion and it was traced in all of the previously examined salts with a range of nitrogen-rich cations (Domasevitch and Ponomarova, 20110). Domasevitch and Ponomarova (20110). That the resulting networks are ionic may find further applications to the synthesis of inorganic nitro-rich salts, based upon Li⁺, Rb⁺, Cs⁺, Sr²⁺, Ba²⁺ and other s- and p-block cations, which are a new generation of ‘green’ pyrotechnic formulations (Steinhauser & Klapötke, 2008).

Following the above findings, we now describe the synthesis and structure of rubidium and caesium 4-(3,5-dinitropyrazol-4-yl)-3,5-dinitropyrazolates \(M[H(TNBP)]\) \(M = \text{Rb (1) and Cs (2)}\), incorporating the peculiar half-deprotonated bipyrazolate tectons. These materials may give an insight into the development of flame colorants in pyrotechnics: rubidium and caesium compounds exhibit, respectively, purple and orange colors when burned.

2. Structural commentary

The title compounds are isostructural, crystallizing in space group \(C2/c\). The molecular structure of the rubidium salt (1) is shown in Fig. 1, with the unique part comprising one organic anion [H(TNBP)]⁻ (or \(C₃H₅N₅O₈⁻\)) and two cations situated on a crystallographic twofold axis [Rb1] or on a center of inversion [Rb2]. The easy formation of such salts is conditioned by the appreciable acidity of polynitropyrazoles, \(c.f.\) \(pK_a = 3.14\) for 3,5-dinitropyrazole \(v<sub>ersus</sub>\) 14.63 for the parent pyrazole (Janssen et al., 1973), while for the crystallization of singly charged hydrogen bipyrazolate derivatives, the weakly polarizing, large Rb⁺ and Cs⁺ cations are important.

Both unique metal ions exhibit exceptionally high coordination numbers of twelve, which are completed with ten O atoms [Rb−O = 2.8543 (15)−3.6985 (16) Å; Cs−O 3.071 (2)−3.811 (2) Å] and two N atoms of the pyrazole rings \(\text{Rb}−\text{N} = 3.1285 (16)\) and 3.2261 (16) Å; \(\text{Cs}−\text{N} = 3.369 (2)\) and 3.401 (2) Å (Tables 1 and 2). Most of these separations slightly exceed the sum of the corresponding ionic radii \(\text{Rb}^{+} 1.48\) and \(\text{Cs}^{+} 1.61\) Å [which are \(M−O = 3.13\) and 3.28 Å; \(\text{M}−\text{N} = 3.18\) and 3.34 Å for 12-coordinate Rb and Cs ions, respectively (Shannon, 1976)], indicating the weakness of these relatively distal ion–dipole...
N—N bond, which is 1.336 (2) Å for ring fragment [N2—N1—C1 = 110.67 (15); C3—N2—N1 = 105.1 (2)]. The N atoms, which are perceptibly different for the former and not for the latter [106.38 (15) and 107.59 (15)]. In the case of (2), the corresponding geometries are nearly identical for rings A and B [C—N = 1.340 (3)—1.346 (3) Å; N2—N1—C1 = 109.8 (2); N3—N4—C6 = 109.6 (2)° and N1—N2—C3 = 104.9 (2); N4—N3—C4 = 105.1 (2)°]. This situation agrees with the disorder of the H atoms between two positions [at the N1 or N4 carrier atoms] within the N—H···N hydrogen bond in (2) as discussed below.

In both structures, the [H(TNBP)]− anions display twisted conformations, with the dihedral angles between the rings being 42.99 (8) and 44.86 (10)° for (1) and (2), respectively. These angles, however, are unusually small. For example, interactions. This may be best related to the bonding in the ionic salts with polyammonium cations, since they are frequently seen in conventional donor sites. For example, in caesium picrate, the cations display a comparable 12-fold coordination and a wide spread of Cs—O separations of 3.028 (3)—3.847 (2) Å (Schouten et al., 1990). The coordination polyhedra of the two unique cations are very similar and represent essentially distorted icosahedra (Fig. 2).

Two of the main geometrical parameters of the organic anions are very similar to those of the parent [H2(TNBP)]+ anions, which maintain supramolecular boxes with a small internal cavity for the cation (Fig. 3). It is notable that all of the eight O atoms present and the two pyrazole N atoms coordinate to the metal ions.

The main geometrical parameters of the organic anions are very similar to those of the parent [H2(TNBP)]+ (Domasevitch et al., 2019). In the case of (1), the protolytic inequivalency of two pyrazole halves is reflected by the ring C—N distances, which are almost the same for anionic ring A (atoms C4/C5/C6/N3/N4) [N3—C4 = 1.343 (2) and N4—C6 1.348 (2) Å] and are slightly differentiated for the neutral ring B (C1/C2/C3/N1/N2) [N1—C1 1.348 (2) and N2—C3 1.331 (2) Å] (Fig. 1). In addition, the deprotonation causes slight elongation of the N—N bond, which is 1.336 (2) Å for ring B and 1.347 (2) Å for ring A. Even more sensitive parameters are the bond angles at the N atoms, which are perceptibly different for the former fragment [N2—N1—C1 = 110.67 (15); C3—N2—N1 = 104.29 (15)°], being much closer for the latter [106.38 (15) and 107.59 (15)°].

3. Supramolecular features

The ionic structures of the title compounds may be regarded as three-dimensional networks, which are related to the structure of CsCl. The metal ions themselves constitute a distorted primitive cubic framework with the cells representing elongated prisms [the M—M edges are 5.2560 (3), 6.5962 (3), 8.8395 (8) and 5.4775 (12), 6.3932 (5), 9.1482 (12) Å for (1) and (2), respectively]. Every such cell is populated with the organic anion and, conversely, every cation resides inside the distorted prismatic box of eight anions (Figs. 3 and 4).

Beyond Coulombic attraction, the principal supramolecular interaction is strong and directional N—H···N hydrogen bonding between the pyrazole and pyrazolato halves of...
and 163 with energetic polynitro derivatives. In fact, the conjugate highly reliable supramolecular synthon for crystal engineering involving the conjugate acid (pyrazole-NH) and base (pyrazolate-N) sites is a very rare, if not the only, example of a translation-related anions \[\text{N}1\cdots\text{N}4\text{iv} = 2.785 (2)\] and \[\text{N}1\cdots\text{N}4\text{iv} = 2.832 (3) \quad \text{Å}\] of the anionic chains) showing the organic layers, which are separated by layers of metal cations (Fig. 5). There are two kinds of weaker interactions, which facilitate close packing of the chains. The first of these is identified by close N3\cdotsN6\text{ii} and N2\cdotsN7\text{ii} contacts [the shortest of 2.990 (3) Å] originating in the situation of the pyrazole N atoms almost exactly above the NO2 N atoms (Table 3). This peculiar lone pair–π-hole interaction occurs instead of the more common NO2/NO2 bonding (Bauzá et al., 2017), which is also relevant for the structure of \([\text{H}_2(\text{TNBP})]\) itself (Domasevitch et al., 2019). One can note that extensive ion-dipole interactions \(M\cdots\text{O}_2\text{N}\) in (1) and (2) mitigate against mutual interactions of nitro groups, which are totally eliminated from the suite of supramolecular bonds. The interactions are relevant for many organic species, e.g., carboxylates (Speakman, 1972) and oximes (Domasevitch et al., 1998), being often the most crucial bonding for the crystal patterns. With the aid of such a synthon, the assembly of the organic subtopology of lower dimensionality is possible in a very rational and predictable fashion and the title structures exactly follow the motifs of previously examined \(\text{NH}_3\text{OH}^+\) and 3,3′,5,5′-tetramethyl-4,4′-bipyrazolium \([\text{H}(\text{TNBP})]^+\) salts (Gospodinov et al., 2020).

The above hydrogen-bonded chains associate to yield layers lying parallel to the \(ac\) plane and the latter are separated by the layers of metal cations (Fig. 5). There are two kinds of weaker interactions, which facilitate close packing of the chains. The first of these is identified by close N3\cdotsN6\text{ii} and N2\cdotsN7\text{ii} contacts [the shortest of 2.990 (3) Å] originating in the situation of the pyrazole N atoms almost exactly above the NO2 N atoms (Table 3). This peculiar lone pair–π-hole interaction occurs instead of the more common NO2/NO2 bonding (Bauzá et al., 2017), which is also relevant for the structure of \([\text{H}_2(\text{TNBP})]\) itself (Domasevitch et al., 2019). One can note that extensive ion-dipole interactions \(M\cdots\text{O}_2\text{N}\) in (1) and (2) mitigate against mutual interactions of nitro groups, which are totally eliminated from the suite of supramolecular bonds. The interactions are relevant for many organic species, e.g., carboxylates (Speakman, 1972) and oximes (Domasevitch et al., 1998), being often the most crucial bonding for the crystal patterns. With the aid of such a synthon, the assembly of the organic subtopology of lower dimensionality is possible in a very rational and predictable fashion and the title structures exactly follow the motifs of previously examined \(\text{NH}_3\text{OH}^+\) and 3,3′,5,5′-tetramethyl-4,4′-bipyrazolium \([\text{H}(\text{TNBP})]^+\) salts (Gospodinov et al., 2020).

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second type of interchain interaction is stacking between pairs of inversion-related pyrazole and pyrazolate rings (Fig. 6), with the O7 and N5 atoms situated nearly above the centroids of the rings $A^{iii}$ and $B^{xiii}$, respectively [symmetry codes: (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (xiii) $-x + \frac{1}{2}, -y - \frac{1}{2}, -z$] (Table 4). As a result of the inversion symmetry of the stacks, the alignment of two polar hydrogen-bonded chains in (1) is antiparallel, while the above lone pair–π-hole interactions support coherent alignment of the contributing chains (Fig. 6). This results in pairing of the chains possessing identical polarities (Fig. 5). In the structure of (2), the polarity of the chains is eliminated because of the disorder of the H atoms in the N–H···N/ N···H–N bonds.

4. Hirshfeld analysis

The supramolecular interactions in the title structures were also assessed by Hirshfeld surface analysis (Spackman & Byrom, 1997; McKinnon et al., 2004; Hirshfeld, 1977; Spackman & McKinnon, 2002) performed with Crystal-Explorer17 (Turner et al., 2017). The contributions of different kinds of interatomic contacts to the Hirshfeld surfaces of the individual anions are listed in Table 5 and the fingerprint plots for (1) are shown in Fig. 7. The most significant contributors are O···O contacts (37.4%), while the fraction of O,N···Rb (15.4%) is relatively modest due to the larger lengths of the ion–dipole interactions. The shortest O···O separation on the plot of $\sim 2.8$ Å corresponds to the contact O1···O8 $\equiv$ 2.741 (2) Å [2.732 (3) Å in (2); symmetry code (xiii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$]. We note that slight contraction of the O···M fraction in the case of $M = \text{Rb}$ [13.6% for (1) and 13.0% for (2)] coincides with a larger contribution of less favorable O···O contacts [37.4% for (1) and 35.5% for (2)]. This may be an additional factor destabilizing the structure: the crystals of (1) eventually decompose under the mother solution, unlike the stable Cs analogue. The lone pair–π-hole pyrazole-NO2 interactions generate 5.3% (1) and 6.3% (2) of the contacts of pairing.

Table 4

Geometry of stacking interactions involving nitro and pyrazole groups (Å, °) in (1) and (2).

| Compound | Atom   | Ring          | Atom ·· Cg | Atom ·· plane | ψ      |
|----------|--------|---------------|------------|---------------|--------|
| (1)      | O7     | (C4C5O(N3N4)) | 3.265 (3)  | 3.262 (2)     | 87.5 (2) |
|          | N5     | (C1C2C3N1)   | 3.541 (3)  | 3.526 (3)     | 84.7 (2) |
| (2)      | O7     | (C4C5O(N3N4)) | 3.240 (3)  | 3.232 (3)     | 86.0 (3) |
|          | N5     | (C1C2C3N1)   | 3.448 (3)  | 3.389 (3)     | 79.4 (3) |

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

Figure 7

Two-dimensional fingerprint plots for the individual anions in (1), and delineated into the principal contributions of O,N···Rb, O···O, N···N, O···N/N···O, O···C/C···O, N···C/C···C, N···H/H···N and O···H/H···O contacts. Other contacts are C···H/H···C (1.5%) and C···C (1.0%).

Table 5

Contributions of the different kinds of the contacts (%) to the Hirshfeld surfaces of individual anions in (1) and (2).

| Contact | (1) | (2) |
|---------|-----|-----|
| O···M   | 13.0| 13.6|
| N···M   | 2.4 | 2.2 |
| O···O   | 37.4| 35.5|
| N···N   | 5.3 | 6.3 |
| C···C   | 1.0 | 0.7 |
| O···N/N···O | 15.8 | 16.2 |
| O···C/C···O | 3.8 | 5.4 |
| N···C/C···N | 7.5 | 6.6 |
| N···H/H···N | 6.9 | 6.6 |
| O···H/H···O | 5.4 | 5.2 |
| C···H/H···C | 1.5 | 1.7 |

Note: (a) For the two-dimensional plots for (1), see Fig. 7.
the Hirshfeld surfaces, with the shortest N···N = 2.9 Å. The nature of the O···N/N···O and N···C/C···N contacts [in total 23.3% (1) and 22.8% (2)] is similar, since they correspond to the stacking of pyrazole and NO2 groups with shortest O···N and N···C distances of 3.2 and 3.3 Å, respectively. However, there are no pairs of the features that are characteristic for the mutual O···N/N···O interactions of NO2 groups themselves (Domasevitch et al., 2020). The contributions of the O···H/H···O and N···H/H···N contacts are comparable and perceptible [5.4 and 6.9% for (1) and 5.2 and 6.6% for (2)], but only the latter correspond to hydrogen bonding, as is reflected in the plots. These bonds are responsible for a pair of very sharp features pointing to the lower left, with a shortest contact of 1.9 Å, whereas O···H/H···O contacts are identified only with a diffuse collection of points between the above features and with a shortest contact of 2.8 Å.

5. Synthesis and crystallization

3,3’,5,5’-Tetranitro-4,4’-bipyrazole [H2(TNBP)] was synthesized in 92% yield by nitration of 4,4’-bipyrazole in mixed acids and then crystallized from water as a monohydrate (Domasevitch et al., 2019).

To prepare the Rb salt (1), 0.332 g (1.0 mmol) of H2(TNBP)-H2O was added to a solution of 0.116 g (0.5 mmol) of Rb2CO3 in 8 ml of water and the mixture was heated at 353–363 K until total dissolution was observed. The solution was cooled to room temperature and left for a few hours for crystallization. Pale-yellow crystals of Rb[H(TNBP)] were isolated in a yield of 0.325 g (82%) and dried in air. The compound is unstable when stored under the reaction solution as the initially formed crystals dissolve in a period of 10–15 d and colorless H2(TNBP)-H2O deposits. In a similar way, the reaction of 0.332 g (1.0 mmol) of H2(TNBP)-H2O and 0.163 g (0.5 mmol) of Cs2CO3 in 8 ml of water gives 0.415 g (93%) of pale-yellow Cs[H(TNBP)] (2). Unlike (1), this material is stable under the mother solution. Similar reactions with Na2CO3 and K2CO3 did not afford any hydrogen bipyrazolates and led to soluble M2[TNBPA] (M = Na, K) and precipitation of the excess amount of H2(TNBP)-H2O.

Analysis (%) calculated for (1), C8H7N5O5Rb: C 18.08, H 0.25, N 28.12; found: C 17.93, H 0.44, N 28.49. IR (KBr, cm−1): 590 w, 708 w, 838 m, 854 s, 996 m, 1024 m, 1308 s, 1352 vs, 1432 m, 1490 vs, 1500 m, 1556 vs, 1636 w, 3448 br.

Analysis (%) calculated for (2), C8H7N5O5Cs: C 16.15, H 0.23, N 25.13; found: C 16.01, H 0.38, N 28.11. IR (KBr, cm−1): 516 w, 586 m, 708 m, 838 s, 852 s, 994 s, 1022 m, 1170 w, 1306 s, 1324 s, 1350 vs, 1396 vs, 1432 s, 1488 vs, 1512 vs, 1544 vs, 1634 m, 3024 br, 3442 br.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. The hydrogen atoms were located and then refined as riding with N–H = 0.87 Å and Uiso(H) =
1.5U_{eq}(N). For (2), the H atom is equally disordered over two positions corresponding to the N1 and N4 carrier atoms.

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Isostructural rubidium and caesium 4-(3,5-dinitropyrazol-4-yl)-3,5-dinitropyrazolates: crystal engineering with polynitro energetic species

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Computing details
For both structures, data collection: IPDS Software (Stoe & Cie, 2000); cell refinement: IPDS Software (Stoe & Cie, 2000); data reduction: IPDS Software (Stoe & Cie, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2018/1 (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: WinGX (Farrugia, 2012).

Poly[μ₄-4-(3,5-dinitropyrazol-4-yl)-3,5-dinitropyrazol-1-ido]rubidium] (1)

Crystal data
[Rb(C₆H₇N₈O₈)]
Mr = 398.62
Monoclinic, C₂/c
a = 19.4400 (15) Å
b = 8.6070 (4) Å
h = 16.9577 (10) Å
β = 115.264 (7)°
V = 2435.8 (3) Å³
Z = 8

Data collection
Stoe IPDS
diffractometer
Radiation source: fine-focus sealed tube
φ oscillation scans
Absorption correction: numerical
[X-RED (Stoe & Cie, 2001) and X-SHAPE (Stoe & Cie, 1999)]
Tmin = 0.672, Tmax = 0.789

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.026
wR(F²) = 0.055
S = 0.89
2890 reflections
210 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
w = 1/σ(F²) + (0.0326P)²
where P = (F² + 2Fc²)/3
(Δ/σ)max < 0.001
Δρmax = 0.37 e Å⁻³
Δρmin = −0.39 e Å⁻³

F(000) = 1552
Dc = 2.174 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 8000 reflections
θ = 2.3–27.9°
μ = 4.13 mm⁻¹
T = 213 K
Prism, yellow
0.20 × 0.16 × 0.14 mm

Tmin = 0.672, Tmax = 0.789
9925 measured reflections
2890 independent reflections
2186 reflections with I > 2σ(I)
Rint = 0.033
θmax = 27.9°, θmin = 2.3°
h = −25→25
k = −10→11
l = −20→20

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**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.

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

| Atom | x     | y     | z     | Uiso* / Ueq |
|------|-------|-------|-------|-------------|
| Rb1  | 0.50000 | 0.39279 (3) | 0.250000 | 0.02840 (9) |
| Rb2  | 0.00000 | 0.50000 | 0.00000 | 0.03230 (9) |
| O1   | 0.38330 (9) | -0.38304 (18) | 0.16106 (14) | 0.0422 (5) |
| O2   | 0.38489 (9) | -0.14611 (18) | 0.11639 (13) | 0.0344 (4) |
| O3   | 0.03697 (9) | -0.16032 (19) | 0.06215 (16) | 0.0490 (5) |
| O4   | 0.10681 (9) | 0.03244 (17) | 0.13792 (13) | 0.0347 (4) |
| O5   | 0.45319 (8) | 0.09854 (18) | 0.30718 (12) | 0.0329 (4) |
| O6   | 0.37797 (9) | -0.09294 (16) | 0.29580 (11) | 0.0301 (4) |
| O7   | 0.13123 (9) | 0.34370 (17) | -0.01293 (13) | 0.0344 (4) |
| O8   | 0.12218 (8) | 0.09417 (17) | -0.03095 (11) | 0.0280 (3) |
| N1   | 0.23222 (9) | -0.36612 (17) | 0.10737 (13) | 0.0199 (4) |
| H1   | 0.247444 | -0.461154 | 0.107308 | 0.030* |
| N2   | 0.16218 (9) | -0.32601 (19) | 0.09532 (13) | 0.0210 (4) |
| N3   | 0.33470 (9) | 0.27100 (18) | 0.19547 (13) | 0.0207 (4) |
| N4   | 0.26946 (9) | 0.31935 (17) | 0.12643 (13) | 0.0200 (4) |
| N5   | 0.53538 (7) | -0.25662 (18) | 0.13349 (12) | 0.0212 (4) |
| N6   | 0.09790 (10) | -0.0935 (2) | 0.10011 (14) | 0.0266 (4) |
| N7   | 0.39083 (9) | 0.03467 (19) | 0.27152 (13) | 0.0218 (4) |
| N8   | 0.15509 (9) | 0.21089 (19) | 0.01062 (13) | 0.0206 (4) |
| C1   | 0.27606 (10) | -0.2391 (2) | 0.11965 (14) | 0.0175 (4) |
| C2   | 0.23545 (10) | -0.1061 (2) | 0.11814 (14) | 0.0161 (4) |
| C3   | 0.16475 (10) | -0.1719 (2) | 0.10251 (15) | 0.0181 (4) |
| C4   | 0.32927 (10) | 0.1159 (2) | 0.19966 (14) | 0.0177 (4) |
| C5   | 0.26131 (10) | 0.0553 (2) | 0.13416 (14) | 0.0158 (4) |
| C6   | 0.22651 (10) | 0.1926 (2) | 0.08941 (14) | 0.0167 (4) |

**Atomic displacement parameters (Å²)**

| Atom | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|------|-----|-----|-----|-----|-----|-----|
| Rb1  | 0.01707 (13) | 0.01962 (14) | 0.0442 (2) | 0.000 | 0.00897 (13) | 0.000 |
| Rb2  | 0.02226 (15) | 0.03355 (17) | 0.0307 (2) | 0.00090 (12) | 0.00132 (12) | -0.01165 (14) |
| O1   | 0.0311 (8) | 0.0188 (8) | 0.0702 (14) | 0.0128 (6) | 0.0153 (9) | 0.0038 (8) |
| O2   | 0.0284 (8) | 0.0279 (8) | 0.0533 (12) | -0.0005 (6) | 0.0234 (8) | 0.0034 (8) |
| O3   | 0.0212 (8) | 0.0283 (9) | 0.0941 (17) | -0.0011 (7) | 0.0214 (9) | 0.0036 (9) |
| O4   | 0.0411 (9) | 0.0214 (8) | 0.0519 (12) | 0.0071 (7) | 0.0299 (9) | -0.0003 (7) |
| O5   | 0.0206 (7) | 0.0336 (8) | 0.0327 (10) | -0.0044 (6) | 0.0001 (7) | 0.0048 (7) |
| O6   | 0.0375 (8) | 0.0155 (7) | 0.0272 (10) | -0.0001 (6) | 0.0040 (7) | 0.0046 (6) |
| O7   | 0.0313 (8) | 0.0190 (7) | 0.0470 (12) | 0.0121 (6) | 0.0111 (8) | 0.0127 (7) |
| O8   | 0.0225 (7) | 0.0231 (8) | 0.0305 (10) | -0.0046 (6) | 0.0037 (6) | 0.0008 (7) |

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Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°) |
|-----------------------|--------------|-----------|
| Rb1—O1 i              | 2.8543 (15)  | O1—N5     | 1.221 (2) |
| Rb1—O1 ii             | 2.8543 (15)  | O2—N5     | 1.219 (2) |
| Rb1—O5                | 2.9673 (16)  | O3—N6     | 1.220 (2) |
| Rb1—O5 iii            | 2.9673 (16)  | O4—N6     | 1.219 (2) |
| Rb1—N3                | 3.1285 (16)  | O5—N7     | 1.228 (2) |
| Rb1—N3 iii            | 3.1285 (16)  | O6—N7     | 1.227 (2) |
| Rb1—O8 iv             | 3.3074 (16)  | O7—N8     | 1.231 (2) |
| Rb1—O8 v              | 3.3074 (16)  | O8—N8     | 1.225 (2) |
| Rb1—O3 vii            | 3.424 (2)    | N1—N2     | 1.336 (2) |
| Rb1—O3 viii           | 3.424 (2)    | N1—C1     | 1.348 (2) |
| Rb1—O4 vi             | 3.4942 (16)  | N1—H1     | 0.8700    |
| Rb1—O4 vii            | 3.4942 (16)  | N2—C3     | 1.331 (2) |
| Rb2—O5 viii           | 2.9616 (17)  | N3—C4     | 1.343 (2) |
| Rb2—O5 ix             | 2.9616 (17)  | N3—N4     | 1.347 (2) |
| Rb2—O7 x              | 2.9690 (15)  | N4—C6     | 1.348 (2) |
| Rb2—O7               | 2.9690 (15)  | N5—C1     | 1.440 (2) |
| Rb2—O3 x              | 3.0743 (17)  | N6—C3     | 1.450 (2) |
| Rb2—O3 ii             | 3.0743 (17)  | N7—C4     | 1.441 (2) |
| Rb2—N2 x              | 3.2261 (16)  | N8—C6     | 1.435 (3) |
| Rb2—N2 ii             | 3.2261 (16)  | C1—C2     | 1.384 (3) |
| Rb2—O6 viii           | 3.2275 (16)  | C2—C3     | 1.406 (3) |
| Rb2—O6 vii            | 3.2275 (16)  | C2—C5     | 1.462 (2) |
| Rb2—O2 v              | 3.6985 (16)  | C4—C5     | 1.393 (3) |
| Rb2—O2 vi             | 3.6985 (16)  | C5—C6     | 1.399 (3) |

*Note: The table continues with similar entries for other bonds and angles.*
| Bond | Distance (Å) | Estimated Error | Bond | Distance (Å) | Estimated Error |
|------|-------------|-----------------|------|-------------|----------------|
| O1—Rb1—N3 | 150.29 (5) |                | N2—Rb2—O6 | 120.91 (4) |                |
| O1—Rb1—N3 | 65.44 (5)  |                | O5—Rb2—O6 | 139.46 (4) |                |
| O5—Rb1—N3 | 52.18 (4)  |                | O5—Rb2—O6 | 40.54 (4)  |                |
| O5—Rb1—N3 | 92.36 (4)  |                | O7—Rb2—O6 | 108.72 (5) |                |
| O1—Rb1—N3 | 65.44 (5)  |                | O1—Rb1—N3 | 71.28 (5)  |                |
| O1—Rb1—N3 | 150.29 (5) |                | O1—Rb1—N3 | 93.66 (5)  |                |
| O5—Rb1—N3 | 92.36 (4)  |                | O3—Rb1—O6 | 86.34 (5)  |                |
| O5—Rb1—N3 | 52.18 (4)  |                | O3—Rb1—O6 | 120.91 (4) |                |
| N3—Rb1—N3 | 140.85 (6) |                | N2—Rb2—O6 | 59.09 (4)  |                |
| O1—Rb1—O8 | 52.19 (5)  |                | O6—Rb2—O6 | 180.00 (7) |                |
| O1—Rb1—O8 | 124.56 (5) |                | O5—Rb2—O2 | 63.14 (4)  |                |
| O5—Rb1—O8 | 82.76 (4)  |                | O5—Rb2—O2 | 116.86 (4) |                |
| O5—Rb1—O8 | 100.60 (4) |                | O7—Rb2—O2 | 127.24 (4) |                |
| N3—Rb1—O8 | 119.65 (4) |                | O1—Rb1—O8 | 52.75 (4)  |                |
| N3—Rb1—O8 | 61.84 (4)  |                | O3—Rb2—O2 | 105.45 (5) |                |
| O1—Rb1—O8 | 124.56 (5) |                | O3—Rb2—O2 | 74.55 (5)  |                |
| O5—Rb1—O8 | 52.19 (5)  |                | O5—Rb2—O2 | 126.63 (4) |                |
| O5—Rb1—O8 | 100.60 (4) |                | N2—Rb2—O2 | 53.37 (4)  |                |
| N3—Rb1—O8 | 82.76 (4)  |                | O6—Rb2—O2 | 74.96 (4)  |                |
| N3—Rb1—O8 | 61.84 (4)  |                | O6—Rb2—O2 | 105.04 (4) |                |
| O8—Rb1—O8 | 176.11 (5) |                | O5—Rb2—O2 | 63.14 (4)  |                |
| O8—Rb1—O8 | 96.42 (5)  |                | O7—Rb2—O2 | 52.76 (4)  |                |
| O8—Rb1—O8 | 93.94 (5)  |                | O7—Rb2—O2 | 127.25 (4) |                |
| O8—Rb1—O8 | 52.19 (5)  |                | O3—Rb2—O2 | 74.55 (5)  |                |
| O5—Rb1—O8 | 100.60 (4) |                | O3—Rb2—O2 | 105.45 (5) |                |
| O5—Rb1—O8 | 82.76 (4)  |                | N2—Rb2—O2 | 53.37 (4)  |                |
| N3—Rb1—O8 | 119.65 (4) |                | O6—Rb2—O2 | 126.63 (4) |                |
| N3—Rb1—O8 | 61.84 (4)  |                | O6—Rb2—O2 | 105.04 (4) |                |
| O8—Rb1—O8 | 128.33 (4) |                | O2—Rb2—O2 | 74.96 (4)  |                |
| O8—Rb1—O8 | 52.33 (4)  |                | O2—Rb2—O2 | 180.00 (3) |                |
| O1—Rb1—O3 | 93.94 (5)  |                | N5—O1—Rb1 | 158.96 (13) |                |
| O5—Rb1—O3 | 111.58 (4) |                | N6—O3—Rb1 | 130.77 (13) |                |
| O5—Rb1—O3 | 53.44 (4)  |                | N6—O3—Rb1 | 91.12 (15)  |                |
| O5—Rb1—O3 | 106.56 (4) |                | Rb2—O3—Rb1 | 107.84 (12) |                |
| O5—Rb1—O3 | 68.00 (4)  |                | N6—O4—Rb1 | 87.86 (12)  |                |
| O5—Rb1—O3 | 111.58 (4) |                | N6—O4—Rb1 | 99.33 (12)  |                |
| O5—Rb1—O3 | 68.00 (4)  |                | O7—O5—Rb1 | 127.55 (12) |                |
| O5—Rb1—O3 | 106.56 (4) |                | Rb2—O5—Rb1 | 124.88 (5)  |                |
| O8—Rb1—O3 | 52.33 (4)  |                | O7—O6—Rb2 | 86.64 (11)  |                |
| O8—Rb1—O3 | 128.33 (4) |                | N8—O7—Rb2 | 128.40 (13) |                |
| O8—Rb1—O3 | 164.66 (6) |                | N8—O8—Rb1 | 121.64 (12) |                |
| O8—Rb1—O3 | 60.41 (5)  |                | N2—N1—C1  | 110.67 (15) |                |
| O8—Rb1—O3 | 91.65 (5)  |                | N2—N1—H1  | 124.7  |                |
| O8—Rb1—O3 | 141.47 (4) |                | C1—N1—H1  | 124.7  |                |
| O5—Rb1—O4 | 78.75 (4)  |                | C3—N2—N1  | 104.29 (15) |                |
| O5—Rb1—O4 | 137.39 (5) |                | C3—N2—Rb2 | 119.80 (12) |                |
| O5—Rb1—O4 | 59.64 (4)  |                | N1—N2—Rb2 | 132.66 (12) |                |
| O8—Rb1—O4 | 102.96 (4) |                | N1—N2—Rb2 | 132.66 (12) |                |
| O8—Rb1—O4 | 75.66 (4)  |                | N1—N2—Rb2 | 132.66 (12) |                |
| Bond                | Distance (Å)  | Torsion (°)  |
|---------------------|---------------|-------------|
| O3vii—Rb1—O4vii    | 153.75 (4)    | C4—N3—N4    | 106.38 (15) |
| O1i—Rb1—O4viii     | 91.65 (5)     | C4—N3—Rb1   | 114.35 (12) |
| O1i—Rb1—O4vii      | 60.41 (5)     | N4—N3—C6    | 128.37 (12) |
| O5—Rb1—O4viii      | 78.75 (4)     | N3—N4—C6    | 107.59 (15) |
| O5viii—Rb1—O4vii   | 141.47 (4)    | O2—N5—O1    | 125.25 (17) |
| N3—Rb1—O4vii       | 59.64 (4)     | O2—N5—C1    | 118.13 (15) |
| N3—Rb1—O4vii       | 137.39 (5)    | O1—N5—C1    | 116.61 (16) |
| O8—Rb1—O4vii       | 75.66 (4)     | O4—N6—O3    | 124.73 (18) |
| O8—Rb1—O4viii      | 102.96 (4)    | O4—N6—C3    | 117.74 (17) |
| O3—Rb1—O4vii       | 153.75 (4)    | O3—N6—C3    | 117.50 (18) |
| O3—Rb1—O4vii       | 36.38 (4)     | O4—N6—Rb1   | 72.68 (11)  |
| O4v—Rb1—O4vii      | 139.76 (5)    | O3—N6—Rb1   | 69.40 (14)  |
| O5viii—Rb2—O5vii   | 180.00 (8)    | C3—N6—Rb1   | 132.87 (13) |
| O5viii—Rb2—O7v     | 108.32 (4)    | O6—N7—O5    | 123.15 (18) |
| O5viii—Rb2—O7v     | 71.68 (4)     | O6—N7—C4    | 118.54 (16) |
| O5vii—Rb2—O7       | 71.68 (4)     | O5—N7—C4    | 118.29 (16) |
| O5vii—Rb2—O7       | 108.32 (4)    | O6—N7—Rb2   | 72.15 (11)  |
| O5vii—Rb2—O7       | 180.0         | O5—N7—Rb2   | 59.69 (11)  |
| O5vii—Rb2—O3v      | 57.45 (5)     | C4—N7—Rb2   | 146.67 (12) |
| O5vii—Rb2—O3v      | 122.55 (5)    | O8—N8—O7    | 123.57 (18) |
| O7v—Rb2—O3v        | 111.42 (4)    | O8—N8—C6    | 118.40 (15) |
| O7—Rb2—O3v         | 68.58 (4)     | O7—N8—C6    | 118.00 (17) |
| O5viii—Rb2—O3viii  | 122.55 (5)    | N1—C1—C2    | 110.36 (16) |
| O5vii—Rb2—O3vii    | 57.45 (5)     | N1—C1—N5    | 119.62 (15) |
| O7—Rb2—O3v         | 68.58 (4)     | C2—C1—N5    | 130.01 (16) |
| O3v—Rb2—O3ii       | 111.42 (4)    | C1—C2—C3    | 100.20 (16) |
| O3v—Rb2—O3ii       | 180.00 (10)   | C1—C2—C5    | 129.17 (17) |
| O5viii—Rb2—N2v     | 64.39 (4)     | C3—C2—C5    | 130.53 (17) |
| O5viii—Rb2—N2v     | 115.61 (4)    | N2—C3—C2    | 114.47 (16) |
| O7v—Rb2—N2v        | 63.20 (4)     | N2—C3—N6    | 117.47 (16) |
| O7—Rb2—N2v         | 116.80 (4)    | C2—C3—N6    | 127.90 (17) |
| O3v—Rb2—N2v        | 50.09 (4)     | N3—C4—C5    | 113.82 (17) |
| O3v—Rb2—N2v        | 129.91 (4)    | N3—C4—N7    | 117.80 (17) |
| O5viii—Rb2—N2v     | 115.61 (4)    | C5—C4—N7    | 128.31 (17) |
| O5viii—Rb2—N2v     | 64.39 (4)     | C4—C5—C6    | 99.63 (15)  |
| O7v—Rb2—N2v        | 116.80 (4)    | C4—C5—C2    | 129.27 (17) |
| O7—Rb2—N2v         | 63.20 (4)     | C6—C5—C2    | 131.10 (17) |
| O3v—Rb2—N2v        | 129.91 (4)    | N4—C6—C5    | 112.57 (17) |
| O3v—Rb2—N2v        | 50.09 (4)     | N4—C6—N8    | 119.01 (16) |
| N2v—Rb2—N2v        | 180.0         | C5—C6—N8    | 128.38 (16) |
| O5viii—Rb2—O6viii  | 40.54 (4)     | C1—N1—C2    | −1.3 (2)  |
| C1—N1—N2—C3        | −1.3 (2)      | C1—N2—C2    | 0.0 (2)   |
| C1—N1—N2—Rb2v      | 157.43 (14)   | C5—C2—N2    | −176.6 (2) |
| C4—N3—N4—C6        | −1.0 (2)      | C1—C2—C3    | 175.2 (2) |
| Rb1—N3—N4—C6       | 140.39 (14)   | C5—C2—C3    | −1.4 (4)  |
| Rb1v—O1—N5—O2      | 26.7 (6)      | O4—N6—C2    | 154.3 (2) |
| Rb1v—O1—N5—C1      | −153.8 (4)    | O3—N6—C3    | −24.1 (3) |
Hydrogen-bond geometry (Å, °)

*Symmetry codes: (i) -x+1, y+1, -z+1/2; (ii) x, y+1, z; (iii) -x+1, y, -z+1/2; (iv) x+1/2, -y+1/2, z+1/2; (v) -x+1/2, -y+1/2, -z; (vi) x+1/2, y+1/2, z+1/2; (vii) -x+1/2, y+1/2, -z+1/2; (viii) x-1/2, y+1/2, z-1/2; (ix) -x, -y+1, -z; (x) -x, y-1, -z; (xi) x-1/2, y+1/2, z; (xii) x, y-1, z; (xiii) x-1/2, y-1/2, z; (xiv) -x+1/2, y-1/2, -z+1/2.*

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**Poly[[μ₄-4-(3,5-dinitropyrazol-4-yl)-3,5-dinitropyrazol-1-ido]caesium] (2)**

**Crystal data**

\[\text{Cs(C}_6\text{HN}_8\text{O}_8)\]  

\(a = 19.944 \ (2) \ \text{Å} \)  

\(b = 8.6307 \ (7) \ \text{Å} \)  

Monoclinic, \(C2/c\)  

\(c = 16.2083 \ (17) \ \text{Å} \)  

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**supporting information**

| Rb₁xiii—O₄—N₆—O₃ | 48.3 (2) | Rb₁xiii—N₆—C₃—N₂ | 62.6 (3) |
|-------------------|----------|-------------------|----------|
| Rb₁xiii—O₄—N₆—C₃ | -129.88 (17) | O₄—N₆—C₃—C₂ | -20.8 (3) |
| Rb₂xii—O₃—N₆—O₄ | -164.56 (17) | O₃—N₆—C₃—C₂ | 160.8 (2) |
| Rb₁xiii—O₃—N₆—C₃ | -49.6 (2) | Rb₁xiii—N₆—C₃—C₂ | -112.5 (2) |
| Rb₂xii—O₃—N₆—C₃ | 13.7 (3) | N₄—N₃—C₄—C₅ | 0.3 (2) |
| Rb₁xiii—N₆—C₃ | 128.59 (17) | Rb₁—N₃—C₄—C₅ | -147.15 (14) |
| Rb₂xii—O₃—N₆—C₃ | -114.92 (19) | N₄—N₃—C₄—N₇ | -177.06 (17) |
| Rb₁xiii—O₃—N₆—Rb₁xiii | 32.5 (2) | Rb₁—N₃—C₄—C₅ | 35.5 (2) |
| Rb₂xii—O₃—N₆—C₃ | 128.59 (17) | Rb₁xiii—N₆—C₃—C₂ | -112.5 (2) |
| Rb₁xiii—O₃—N₆—C₃ | -114.92 (19) | N₄—N₃—C₄—N₇ | -177.06 (17) |
| Rb₂xii—O₃—N₆—C₃ | 32.5 (2) | Rb₁xiii—N₆—C₃—C₂ | -112.5 (2) |
| Rb₁—O₅—N₇—O₆ | -36.3 (2) | O₅—N₇—C₄—C₅ | -21.3 (3) |
| Rb₁—O₅—N₇—C₃ | 13.7 (3) | Rb₁—N₃—C₄—N₇ | 55.7 (3) |
| Rb₂xiv—O₆—N₇—O₅ | 13.7 (3) | O₆—N₇—C₄—C₅ | -20.3 (3) |
| Rb₂xiv—O₆—N₇—C₃ | 13.7 (3) | O₆—N₇—C₄—C₅ | 161.7 (2) |
| Rb₁—O₅—N₇—C₄ | -7.3 (3) | O₅—N₇—C₄—C₅ | -121.3 (2) |
| Rb₁—O₅—N₇—Rb₁xiii | -149.01 (17) | Rb₂xiv—N₇—C₄—C₅ | -121.3 (2) |
| Rb₁—O₈—N₈—O₇ | 22.7 (3) | N₃—C₄—C₅—C₆ | 0.4 (2) |
| Rb₁—O₈—N₈—C₆ | -155.32 (13) | N₇—C₄—C₅—C₆ | 177.5 (2) |
| Rb₂—O₇—N₈—O₈ | 72.4 (3) | N₃—C₄—C₅—C₂ | -179.85 (19) |
| Rb₂—O₇—N₈—C₆ | -109.63 (17) | N₇—C₄—C₅—C₂ | -2.8 (4) |
| N₂—N₁—C₁—C₂ | 1.4 (2) | C₁—C₂—C₅—C₄ | -41.0 (4) |
| N₂—N₁—C₁—N₅ | -179.72 (17) | C₃—C₂—C₅—C₄ | 134.7 (2) |
| O₂—N₅—C₁—N₁ | 157.8 (2) | C₁—C₂—C₅—C₆ | 138.7 (2) |
| O₁—N₅—C₁—N₁ | -21.7 (3) | C₃—C₂—C₅—C₆ | -45.6 (4) |
| O₂—N₅—C₁—C₂ | -23.6 (3) | N₃—N₄—C₆—C₅ | 1.3 (2) |
| O₁—N₅—C₁—C₂ | 156.9 (2) | N₃—N₄—C₆—N₈ | -176.64 (16) |
| N₁—C₁—C₂—C₃ | -0.8 (2) | C₄—C₅—C₆—N₄ | -1.0 (2) |
| N₅—C₁—C₂—C₃ | -179.5 (2) | C₂—C₅—C₆—N₄ | 179.2 (2) |
| N₁—C₁—C₂—C₅ | 175.8 (2) | C₄—C₅—C₆—N₈ | 176.7 (2) |
| N₅—C₁—C₂—C₅ | -2.9 (4) | C₂—C₅—C₆—N₈ | -3.1 (4) |
| N₁—N₂—C₃—C₂ | 0.8 (2) | O₈—N₈—C₆—N₄ | 168.87 (18) |
| Rb₂xii—N₂—C₃—C₂ | -161.31 (14) | O₇—N₈—C₆—N₄ | -9.2 (3) |
| N₁—N₂—C₃—N₆ | -174.94 (18) | O₈—N₈—C₆—C₅ | -8.7 (3) |
| Rb₂xiv—N₂—C₃—N₆ | 23.0 (2) | O₇—N₈—C₆—C₅ | 173.2 (2) |
\( \beta = 113.766 (8) ^{\circ} \)  
\( V = 2553.4 (5) \, \text{Å}^3 \)  
\( Z = 8 \)  
\( F(000) = 1696 \)  
\( D_\text{x} = 2.321 \, \text{Mg m}^{-3} \)  
Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \, \text{Å} \)  
\( \theta = 2.2-27.8^\circ \)  
\( \mu = 2.97 \, \text{mm}^{-1} \)  
\( T = 213 \, \text{K} \)  
Prism, yellow  
0.20 \times 0.16 \times 0.14 \, \text{mm} 

Data collection  
Stoe IPDS diffractometer  
Radiation source: fine-focus sealed tube  
\( \varphi \) oscillation scans  
\( R_{\text{int}} = 0.042 \)  
Absorption correction: numerical  
\( \theta_{\text{max}} = 27.8^\circ, \theta_{\text{min}} = 2.2^\circ \)  
\( h = -20 \rightarrow 26 \)  
\( k = -11 \rightarrow 11 \)  
\( l = -21 \rightarrow 21 \)  
9014 measured reflections  
2990 independent reflections  
2686 reflections with \( I > 2\sigma(I) \)  
\( \text{Rint} = 0.042 \)  
\( \theta_{\text{max}} = 27.8^\circ, \theta_{\text{min}} = 2.2^\circ \)  
Hydrogen site location: inferred from neighbouring sites  
Extinction correction: \textit{SHELXL2018/1}  
Extinction coefficient: 0.00151 (14)  

Special details  
\textbf{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.

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

| x          | y          | z          | U_{iso}/U_{eq} | Occ. (<1) |
|------------|------------|------------|----------------|-----------|
| Cs1        | 0.500000   | 0.42703 (3)| 0.250000       | 0.03031 (9)|
| Cs2        | 0.000000   | 0.500000   | 0.000000       | 0.04080 (10)|
| O1         | 0.36906 (14)| -0.3754 (3)| 0.1294 (2)     | 0.0536 (7)|
| O2         | 0.38087 (12)| -0.1274 (2)| 0.12176 (15)  | 0.0369 (5)|
| O3         | 0.04269 (12)| -0.1420 (3)| 0.07349 (18)  | 0.0460 (6)|
| O4         | 0.11168 (14)| 0.0488 (2) | 0.14521 (17)  | 0.0391 (5)|
| O5         | 0.44367 (12)| 0.1085 (2) | 0.29706 (15)  | 0.0379 (5)|
| O6         | 0.36857 (13)| -0.0765 (2)| 0.29226 (14)  | 0.0351 (5)|
| O7         | 0.13940 (12)| 0.3610 (2) | -0.01257 (15) | 0.0391 (5)|
| O8         | 0.12142 (13)| 0.1123 (2) | -0.02282 (14) | 0.0370 (5)|
| N1         | 0.22944 (13)| -0.3511 (2)| 0.10259 (15)  | 0.0260 (5)|
| H1A        | 0.243307   | -0.445633  | 0.099377       | 0.039*    | 0.5|
| N2         | 0.16260 (13)| -0.3095 (2)| 0.09520 (15)  | 0.0267 (5)|

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### Atomic displacement parameters (Å²)

| Atom | \( U^{11} \) | \( U^{22} \) | \( U^{33} \) | \( U^{12} \) | \( U^{13} \) | \( U^{23} \) |
|------|------------|------------|------------|------------|------------|------------|
| Cs1  | 0.02186 (13) | 0.02958 (13) | 0.03945 (15) | 0.000 | 0.01232 (10) | 0.000 |
| Cs2  | 0.02484 (14) | 0.04935 (19) | 0.03776 (16) | −0.00107 (11) | 0.00175 (11) | −0.01535 (12) |
| O1   | 0.0407 (13) | 0.0213 (10) | 0.095 (2) | 0.0120 (10) | 0.0230 (14) | −0.0019 (12) |
| O2   | 0.0366 (12) | 0.0257 (10) | 0.0524 (13) | 0.0006 (9) | 0.0220 (10) | 0.0023 (9) |
| O3   | 0.0277 (11) | 0.0355 (11) | 0.0727 (16) | −0.0002 (10) | 0.0177 (11) | 0.0033 (11) |
| O4   | 0.0456 (13) | 0.0234 (10) | 0.0604 (14) | 0.0040 (9) | 0.0339 (12) | −0.0020 (9) |
| O5   | 0.0276 (11) | 0.0354 (11) | 0.0418 (12) | −0.0014 (8) | 0.0047 (9) | 0.0046 (9) |
| O6   | 0.0440 (13) | 0.0198 (9) | 0.0305 (10) | −0.0020 (8) | 0.0035 (9) | 0.0055 (8) |
| O7   | 0.0395 (12) | 0.0224 (9) | 0.0488 (12) | 0.0106 (9) | 0.0107 (10) | 0.0125 (9) |
| O8   | 0.0369 (12) | 0.0276 (10) | 0.0369 (11) | −0.0045 (9) | 0.0048 (9) | 0.0035 (8) |
| N1   | 0.0305 (11) | 0.0154 (9) | 0.0310 (11) | 0.0029 (9) | 0.0113 (9) | 0.0008 (9) |
| N2   | 0.0312 (12) | 0.0172 (10) | 0.0313 (11) | −0.0004 (9) | 0.0121 (10) | 0.0011 (9) |
| N3   | 0.0305 (12) | 0.0187 (10) | 0.0282 (11) | −0.0016 (9) | 0.0095 (9) | −0.0018 (9) |
| N4   | 0.0311 (12) | 0.0127 (9) | 0.0306 (11) | 0.0031 (8) | 0.0111 (9) | 0.0014 (8) |
| N5   | 0.0272 (12) | 0.0207 (10) | 0.0283 (11) | 0.0053 (9) | 0.0094 (9) | −0.0017 (8) |
| N6   | 0.0314 (13) | 0.0229 (11) | 0.0427 (14) | 0.0025 (10) | 0.0208 (11) | 0.0070 (10) |
| N7   | 0.0299 (12) | 0.0211 (10) | 0.0254 (11) | 0.0028 (9) | 0.0069 (9) | −0.0004 (8) |
| N8   | 0.0268 (12) | 0.0206 (10) | 0.0296 (11) | 0.0045 (9) | 0.0123 (9) | 0.0048 (9) |
| C1   | 0.0282 (13) | 0.0143 (10) | 0.0232 (12) | 0.0035 (9) | 0.0076 (10) | 0.0018 (9) |
| C2   | 0.0288 (13) | 0.0131 (10) | 0.0214 (11) | 0.0013 (10) | 0.0085 (10) | 0.0011 (8) |
| C3   | 0.0284 (13) | 0.0163 (11) | 0.0279 (12) | 0.0015 (10) | 0.0134 (11) | 0.0023 (9) |
| C4   | 0.0274 (13) | 0.0171 (11) | 0.0227 (11) | 0.0022 (10) | 0.0082 (10) | 0.0010 (9) |
| C5   | 0.0267 (13) | 0.0130 (10) | 0.0232 (11) | 0.0020 (9) | 0.0105 (10) | 0.0021 (9) |
| C6   | 0.0265 (13) | 0.0162 (11) | 0.0260 (12) | 0.0052 (9) | 0.0101 (10) | 0.0026 (9) |

### Geometric parameters (Å, °)

- **Cs1—O1**: 3.071 (2)  O2—N5  1.222 (3)
- **Cs1—O1**: 3.071 (2)  O3—N6  1.221 (3)
- **Cs1—O5**: 3.177 (2)  O4—N6  1.225 (3)
- **Cs1—O5**: 3.177 (2)  O5—N7  1.229 (3)
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| Cs1—O3<sup>iv</sup>  | 3.351 (3)    | O6—N7                | 1.224 (3)    |
| Cs1—O3<sup>v</sup>   | 3.351 (3)    | O7—N8                | 1.230 (3)    |
| Cs1—N3                | 3.369 (2)    | O8—N8                | 1.225 (3)    |
| Cs1—N3<sup>iii</sup> | 3.369 (2)    | N1—N2                | 1.338 (3)    |
| Cs1—O4<sup>iv</sup>  | 3.464 (2)    | N1—C1                | 1.342 (3)    |
| Cs1—O4<sup>v</sup>   | 3.464 (2)    | N1—H1A               | 0.8700       |
| Cs1—O8<sup>vi</sup>  | 3.514 (2)    | N2—C3                | 1.340 (3)    |
| Cs1—O8<sup>vii</sup> | 3.514 (2)    | N3—N4                | 1.339 (3)    |
| Cs2—O7<sup>viii</sup>| 3.109 (2)    | N3—C4                | 1.340 (3)    |
| Cs2—O7                | 3.109 (2)    | N4—C6                | 1.346 (3)    |
| Cs2—O5<sup>ix</sup>  | 3.159 (2)    | N4—H1B               | 0.8700       |
| Cs2—O5<sup>v</sup>   | 3.159 (2)    | N5—C1                | 1.439 (4)    |
| Cs2—O3<sup>x</sup>   | 3.297 (2)    | N6—C3                | 1.453 (3)    |
| Cs2—O3<sup>ii</sup>  | 3.297 (2)    | N7—C4                | 1.447 (3)    |
| Cs2—O6<sup>ix</sup>  | 3.396 (2)    | N8—C6                | 1.432 (3)    |
| Cs2—O6<sup>v</sup>   | 3.396 (2)    | C1—C2                | 1.398 (3)    |
| Cs2—N2<sup>x</sup>   | 3.401 (2)    | C2—C3                | 1.404 (4)    |
| Cs2—N2<sup>ii</sup>  | 3.401 (2)    | C2—C5                | 1.458 (3)    |
| Cs2—O2<sup>xi</sup>  | 3.811 (2)    | C4—C5                | 1.396 (4)    |
| Cs2—O2<sup>vi</sup>  | 3.811 (2)    | C5—C6                | 1.399 (3)    |
| O1—N5                 | 1.224 (3)    |                      |              |

| Bond                  | Angle (°)     | Bond                  | Angle (°)     |
|----------------------|--------------|----------------------|--------------|
| O1<sup>i</sup>—Cs1—O1<sup>ii</sup> | 112.57 (9)   | O5<sup>ix</sup>—Cs2—N2<sup>xi</sup> | 60.69 (6)    |
| O1<sup>i</sup>—Cs1—O5<sup>iii</sup> | 109.94 (6)   | O5<sup>v</sup>—Cs2—N2<sup>xi</sup> | 119.31 (6)   |
| O1<sup>i</sup>—Cs1—O5<sup>iii</sup> | 128.30 (6)   | O3<sup>x</sup>—Cs2—N2<sup>xi</sup> | 47.39 (5)    |
| O1<sup>i</sup>—Cs1—O5<sup>iii</sup> | 128.30 (6)   | O3<sup>x</sup>—Cs2—N2<sup>xi</sup> | 132.61 (5)   |
| O1<sup>i</sup>—Cs1—O5<sup>iii</sup> | 109.94 (6)   | O6<sup>x</sup>—Cs2—N2<sup>xi</sup> | 55.26 (5)    |
| O5<sup>iii</sup>—Cs1—O5  | 60.14 (9)    | O6<sup>x</sup>—Cs2—N2<sup>xi</sup> | 124.74 (5)   |
| O1<sup>i</sup>—Cs1—O3<sup>iv</sup> | 101.47 (7)   | O7<sup>iii</sup>—Cs2—N2<sup>xi</sup> | 119.87 (6)   |
| O1<sup>i</sup>—Cs1—O3<sup>iv</sup> | 89.92 (7)    | O7<sup>iii</sup>—Cs2—N2<sup>xi</sup> | 60.13 (6)    |
| O5<sup>iii</sup>—Cs1—O3<sup>iv</sup> | 53.49 (6)    | O5<sup>ix</sup>—Cs2—N2<sup>ii</sup> | 119.31 (6)   |
| O5<sup>iii</sup>—Cs1—O3<sup>iv</sup> | 106.69 (6)   | O5<sup>ix</sup>—Cs2—N2<sup>ii</sup> | 60.69 (6)    |
| O1<sup>i</sup>—Cs1—O3<sup>v</sup> | 89.92 (7)    | O3<sup>x</sup>—Cs2—N2<sup>ii</sup> | 132.61 (5)   |
| O1<sup>i</sup>—Cs1—O3<sup>v</sup> | 101.47 (7)   | O3<sup>x</sup>—Cs2—N2<sup>ii</sup> | 47.39 (5)    |
| O5<sup>iii</sup>—Cs1—O3<sup>v</sup> | 106.69 (6)   | O6<sup>x</sup>—Cs2—N2<sup>ii</sup> | 124.74 (5)   |
| O5<sup>iii</sup>—Cs1—O3<sup>v</sup> | 53.49 (6)    | O6<sup>x</sup>—Cs2—N2<sup>ii</sup> | 55.26 (5)    |
| O3<sup>iv</sup>—Cs1—O3<sup>v</sup> | 159.51 (8)   | N2<sup>x</sup>—Cs2—N2<sup>ii</sup> | 180.0        |
| O1<sup>i</sup>—Cs1—N3 | 151.61 (7)   | O7<sup>iii</sup>—Cs2—O2<sup>xi</sup> | 46.92 (5)    |
| O1<sup>i</sup>—Cs1—N3 | 61.45 (6)    | O7<sup>iii</sup>—Cs2—O2<sup>xi</sup> | 133.09 (5)   |
| O5<sup>iii</sup>—Cs1—N3 | 92.08 (6)    | O5<sup>ix</sup>—Cs2—O2<sup>xi</sup> | 114.79 (5)   |
| O5<sup>iii</sup>—Cs1—N3 | 48.49 (5)    | O5<sup>ix</sup>—Cs2—O2<sup>xi</sup> | 65.21 (5)    |
| O3<sup>iv</sup>—Cs1—N3 | 106.11 (6)   | O3<sup>ii</sup>—Cs2—O2<sup>xi</sup> | 78.04 (6)    |
| O3<sup>iv</sup>—Cs1—N3 | 66.04 (6)    | O3<sup>ii</sup>—Cs2—O2<sup>xi</sup> | 101.96 (6)   |
| O1<sup>i</sup>—Cs1—N3<sup>iii</sup> | 61.45 (6)    | O6<sup>x</sup>—Cs2—O2<sup>xi</sup> | 100.16 (5)   |
| O1<sup>i</sup>—Cs1—N3<sup>iii</sup> | 151.61 (7)   | O6<sup>x</sup>—Cs2—O2<sup>xi</sup> | 79.84 (5)    |
| O5<sup>iii</sup>—Cs1—N3<sup>iii</sup> | 48.49 (5)    | N2<sup>ii</sup>—Cs2—O2<sup>xi</sup> | 54.28 (5)    |
| O5<sup>iii</sup>—Cs1—N3<sup>iii</sup> | 92.08 (6)    | N2<sup>ii</sup>—Cs2—O2<sup>xi</sup> | 125.72 (5)   |
| O3<sup>iv</sup>—Cs1—N3<sup>iii</sup> | 66.03 (6)    | O7<sup>iii</sup>—Cs2—O2<sup>vi</sup> | 133.08 (5)   |
| Bond          | Angle (°) (Standard Deviation) |
|--------------|--------------------------------|
| O3v—Cs1—N3 iv| 106.11 (6)                     |
| N3—Cs1—N3 iv| 137.57 (8)                     |
| O1 iv—Cs1—O4 iv| 66.05 (7)                   |
| O1 iv—Cs1—O4 vi| 93.97 (7)                   |
| O5 vii—Cs1—O4 vi| 77.60 (6)                   |
| O5—Cs1—O4 vi| 137.70 (5)                     |
| O3 vii—Cs1—O4 vi| 36.92 (6)                   |
| O3 viii—Cs1—O4 vi| 155.15 (6)                  |
| N3—Cs1—O4 vi| 138.81 (6)                     |
| N3—Cs1—O4 vi| 57.79 (6)                      |
| O1 iv—Cs1—O4 vi| 36.92 (6)                   |
| O1 iv—Cs1—O4 vi| 138.81 (6)                  |
| O4 vii—Cs1—O4 vi| 144.69 (7)                  |
| O1 iv—Cs1—O4 vi| 140.41 (6)                  |
| O1 iv—Cs1—O4 vi| 48.43 (6)                     |
| O5 vii—Cs1—O4 vi| 79.97 (5)                    |
| O5—Cs1—O4 vi| 90.40 (5)                      |
| O3 vii—Cs1—O4 vi| 52.64 (6)                    |
| O3 vii—Cs1—O4 vi| 124.92 (6)                   |
| N3—Cs1—O4 vi| 90.40 (5)                      |
| N3—Cs1—O4 vi| 90.40 (5)                      |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| N3—Cs1—O4 vi| 52.64 (6)                      |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| O4 vii—Cs1—O4 vi| 124.92 (6)                   |
| O3 vii—Cs1—O4 vi| 52.64 (6)                     |
| O3 vii—Cs1—O4 vi| 116.39 (6)                   |
| O4 vii—Cs1—O4 vi| 79.97 (5)                    |
| Bond | Angle | Value 1 | Value 2 | Value 3 |
|------|-------|---------|---------|---------|
| O5\textsuperscript{iv}—Cs2—O3\textsuperscript{x} | O5\textsuperscript{v}—Cs2—O3\textsuperscript{x} | 54.16 (6) | 125.84 (6) | 73.88 (6) |
| O7\textsuperscript{viii}—Cs2—O3\textsuperscript{ii} | O7—Cs2—O3\textsuperscript{ii} | 106.12 (6) | N1—C1—C2 | 111.4 (2) |
| O5\textsuperscript{ii}—Cs2—O3\textsuperscript{ii} | O5—Cs2—O3\textsuperscript{ii} | 125.84 (6) | N1—C1—N5 | 119.1 (2) |
| O5—Cs2—O3\textsuperscript{ii} | O3\textsuperscript{x}—Cs2—O3\textsuperscript{ii} | 54.16 (6) | C2—C1—N5 | 129.5 (2) |
| O7\textsuperscript{viii}—Cs2—O3\textsuperscript{ii} | O7—Cs2—O6\textsuperscript{ix} | 180.00 (10) | C1—C2—C3 | 99.5 (2) |
| O7—Cs2—O6\textsuperscript{ix} | O7\textsuperscript{viii}—Cs2—O6\textsuperscript{ix} | 68.69 (6) | C1—C2—C5 | 130.2 (3) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 111.31 (6) | C3—C2—C5 | 130.2 (2) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 68.69 (6) | C5—C4—C6 | 119.87 (6) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 141.57 (5) | C1—N1—N2—C3 | −0.7 (3) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 141.57 (5) | C1—N1—N2—C3 | −0.7 (3) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 38.43 (5) | C1—N1—N2—Cs2\textsuperscript{xii} | 158.78 (16) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 38.43 (5) | C1—N1—N2—Cs2\textsuperscript{xii} | 158.78 (16) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 99.19 (5) | O3—N6—C3—N2 | −22.2 (4) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 99.19 (5) | O3—N6—C3—N2 | −22.2 (4) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 80.81 (5) | O3—N6—C3—N2 | −22.2 (4) |
| O7—Cs2—O6\textsuperscript{ix} | O7—Cs2—O6\textsuperscript{ix} | 99.19 (5) | O3—N6—C3—N2 | −22.2 (4) |
| O7—Cs2—N2\textsuperscript{x} | O7—Cs2—N2\textsuperscript{x} | 60.13 (6) | N3—C4—C5 | 114.3 (2) |
| O7—Cs2—N2\textsuperscript{x} | O7—Cs2—N2\textsuperscript{x} | 119.87 (6) | N3—C4—C5 | 114.3 (2) |
| C1—N1—N2—C3 | C1—N1—N2—C3 | −0.7 (3) | C1—N1—N2—C3 | −0.7 (3) |
| C1—N1—N2—C3 | C1—N1—N2—C3 | −0.7 (3) | C1—N1—N2—C3 | −0.7 (3) |
| C1—N1—N2—C3 | C1—N1—N2—C3 | −0.7 (3) | C1—N1—N2—C3 | −0.7 (3) |
| C1—N1—N2—C3 | C1—N1—N2—C3 | −0.7 (3) | C1—N1—N2—C3 | −0.7 (3) |

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N2—N1—C1—N5  \(-178.4 (2)\)  \(C3—C2—C5—C4\)  \(134.1 (3)\)
O2—N5—C1—N1  \(169.4 (2)\)  \(C1—C2—C5—C6\)  \(135.7 (3)\)
O1—N5—C1—N1  \(-9.8 (4)\)  \(C3—C2—C5—C6\)  \(-46.5 (4)\)
O2—N5—C1—C2  \(-9.5 (4)\)  \(N3—N4—C6—C5\)  \(0.5 (3)\)
O1—N5—C1—C2  \(171.4 (3)\)  \(N3—N4—C6—N8\)  \(-176.5 (2)\)
N1—C1—C2—C3  \(-0.4 (3)\)  \(C4—C5—C6—N4\)  \(-0.3 (3)\)
N5—C1—C2—C3  \(178.5 (2)\)  \(C2—C5—C6—N4\)  \(-179.8 (3)\)
N1—C1—C2—C5  \(-3.2 (5)\)  \(C2—C5—C6—N8\)  \(-3.1 (5)\)
N5—C1—C2—C5  \(177.9 (2)\)  \(C4—C5—C6—N8\)  \(176.4 (3)\)
N1—N2—C3—C2  \(0.5 (3)\)  \(O8—N8—C6—N4\)  \(175.1 (2)\)
Cs2\textsuperscript{xii}—N2—C3—C2  \(-161.16 (16)\)  \(O7—N8—C6—N4\)  \(-3.9 (4)\)
N1—N2—C3—N6  \(-175.3 (2)\)  \(O8—N8—C6—C5\)  \(-1.4 (4)\)
Cs2\textsuperscript{xii}—N2—C3—N6  \(23.1 (3)\)  \(O7—N8—C6—C5\)  \(179.6 (3)\)

Symmetry codes: (i) \(-x+1, y+1, -z+1/2\); (ii) \(x, y+1, z\); (iii) \(-x+1, y, -z+1/2\); (iv) \(x+1/2, y+1/2, z\); (v) \(-x+1/2, y+1/2, -z+1/2\); (vi) \(-x+1/2, -y+1/2, -z\); (vii) \(x+1/2, -y+1/2, -z+1/2\); (viii) \(x, -y+1, -z\); (ix) \(x, -y, z\); (x) \(-x, -y, -z\); (xi) \(-x+1/2, y+1/2, z\); (xii) \(-x+1/2, y-1/2, z\); (xiii) \(-x+1/2, y-1/2, -z\); (xiv) \(-x+1/2, -y+1/2, -z\).

### Hydrogen-bond geometry (Å, °)

| \(D—H—A\) | \(D—H\) | \(H—A\) | \(D—A\) | \(D—H—A\) |
|---|---|---|---|---|
| N1—H1A···N4\textsuperscript{xii} | 0.87 | 1.99 | 2.832 (3) | 162 |
| N4—H1B···N1\textsuperscript{ii} | 0.87 | 1.99 | 2.832 (3) | 163 |

Symmetry codes: (ii) \(x, y+1, z\); (xii) \(x, y-1, z\).