Crystal structure of 9-aminoacridinium chloride \(N,N\)-dimethylformamide monosolvate

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9-Aminoacridinium chloride \(N,N\)-dimethylformamide monosolvate, \(\text{C}_13\text{H}_{11}\text{N}_2\text{Cl}^-\cdot\text{C}_7\text{H}_7\text{NO}\), crystallizes in the monoclinic space group \(P2_1/c\). The salt was crystallized from \(N,N\)-dimethylformamide. The asymmetric unit consists of two \(\text{C}_13\text{H}_{11}\text{N}_2\text{Cl}^-\) formula units. The 9-aminoacridinium (9-AA) molecules are protonated with the proton on the N atom of the central ring. This N atom is connected to an \(N,N\)-dimethylformamide molecule by a hydrogen bond. The H atoms of the amino groups create short contacts with two chloride ions. The 9-AA cations in adjacent layers are oriented in an antiparallel manner. The molecules are linked via a network of multidirectional \(\pi-\pi\) interactions between the 9-AA rings, and the whole lattice is additionally stabilized by electrostatic interactions between ions.

1. Chemical context

Aminoacridine (AA) derivatives exhibit antibacterial (Ciric et al., 2011), anticancer (Hassan et al., 2011), antiviral (Kaur & Singh, 2011) and antiprion effects (Villa et al., 2011), as well as other therapeutic properties (Muregi & Ishih, 2010). The synthesis of these compounds and analysis of their interactions is very useful in view of their importance in a wide range of different biological systems (Coupar et al., 1997). Besides, numerous acridine-based derivatives are important for their chemiluminescent ability and their use as chemiluminescent indicators in immunoassays, nucleic acid diagnostics and quantitative assays of biomolecules, such as antigens, antibodies, hormones and enzymes, as well as DNA–RNA structural analyses (Dodeigne, 2000; Becker et al., 1999). Additionally, photochemical reactions for these compounds in different media have been reported (Machulek et al., 2003). AA derivatives are promising analytical agents, since they exhibit relatively high quantum yields of light emission and stability (Adamczyk et al., 1999; Dodeigne, 2000; Renotte et al., 2000; Smith et al., 2009).

9-AA is a fluorescent dye of the family of nitrogen heterocyclic bases. 9-AA has been proposed as a specific fluorescent probe capable of binding the active center of guanidinobenzoatases (GB) (Murza et al., 2000). Interestingly, cellulose nanocomposites based on [Fe(hptrz)](OTs)_2 nanoparticles were effectively doped with 9-AA, resulting in a thermostrophic and thermostable fluorescent material (Nagy et al., 2014). Previous crystallographic studies of some analogues of 9-AA have revealed that while in some members the acridine ring system is nearly planar (Carrell, 1972), in others it is
clamped (Zacharias & Glusker, 1974; Berman & Glusker, 1972; Glusker et al., 1973) with angles of 7–13° between the two outer rings. This publication reports the crystal structure of 9-aminoacridinium chloride \textit{N,N}-dimethylformamide solvate (1:1).

2. Structural commentary

The title compound crystallizes in the monoclinic \textit{P}2\textsubscript{1}/\textit{c} space group, with two 9-AA\textsuperscript{+}\textsuperscript{−}Cl\textsuperscript{−} formula units in the asymmetric unit. As shown in Fig. 1, the molecules are monoionized with the one proton residing on the N atom, N2 or N5, of the central ring.

The amino groups for two 9-aminoacridine molecules do not readily add a proton. The state of ionization is confirmed by both the H-atom positions (located from the difference map) and by the hydrogen bonding as shown in Table 1. The C—NH\textsubscript{2} bonds C1—N1 and C17—N4 are 1.310 (5) and 1.313 (5) \textAA, respectively. These bond lengths are characteristic for a C\textsuperscript{=\textN} double bond that can originate from tautomerism of the cation, as shown on the scheme.

The acridine moieties are nearly planar in the crystalline phase with atoms N2, C1, N1 and N5, C17 and N4 arranged almost linearly (N2···C1—N1 = 176° and N5···C17—N4 = 180°). The dihedral angle between the two outer fused rings is 3.39 (14)° for the molecule containing N2, while the corresponding angle in the molecule containing N5 is 1.18 (15)°. The second value is comparable with that found for acridine (1.2°; Phillips, 1956; Phillips et al., 1960). The 9-AA molecules are almost planar and each of three fused rings taken individually is planar within experimental error.

3. Supramolecular features

The packing of the molecules in the crystal is illustrated in Fig. 2. The crystal structure features N—H···O and N—H···Cl hydrogen bonds (Table 1) as well as \pi–\pi stacking interactions. The 9-AA molecules form layers (Fig. 3), which stack perpendicularly to the \textit{c} axis. There are two types of 9-AA fused rings in the crystal structure, which results in the propagation of layers in a zigzag manner along \textit{b}-axis direction (Fig. 2).

The structure is characterized by the presence of several different kinds of weak interactions, which create a three-dimensional supramolecular network. The atoms H2 and HSA, attached to N2 and N5, form hydrogen bonds to \textit{N,N}-dimethylformamide atoms, O1 and O2, with \(d(\text{N—H}···\text{O}) = 2.723 (5)–2.740 (5) \textAA, \text{N—H}···\text{O} = 175-176°\). The chloride ions are linked via N—H···Cl hydrogen bonds [\(d(\text{N—H}···\text{Cl}) = 3.209 (3)–3.246 (3) \textAA, \text{N—H}···\text{Cl} = 160–163°\)], forming dimers (Fig. 1). In these dimers, the amino groups of the two 9-AA cations and the two halide anions participate in the hydrogen bonding, generating a centrosymmetric \(R\textsuperscript{2}(8)\) supramolecular.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N2—H2···O1 | 0.86 | 1.86  | 2.723 (5) | 176 |
| N4—H4A···Cl2 | 0.86 | 2.40  | 3.225 (3) | 160 |
| N4—H4B···Cl1 | 0.86 | 2.38  | 3.211 (4) | 163 |
| N1—H1A···Cl1 | 0.86 | 2.39  | 3.209 (3) | 160 |
| N1—H1B···Cl2 | 0.86 | 2.42  | 3.246 (3) | 162 |
| N5—H5A···O2 | 0.86 | 1.88  | 2.740 (5) | 175 |

Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are represented by dashed lines. Two amine groups and two chloride ions form a supramolecular \(R\textsuperscript{2}(8)\) synthon.

Figure 2
Crystal packing viewed along the \textit{c} axis. The N—H···Cl and N—H···O interactions are represented by green and red dashed lines, respectively. The \(A\) and \(\text{B}\) acridine molecules are coloured green and blue, respectively.

Figure 3
Layers of 9-AA. \pi–\pi stacking interactions between the 9-aminoacridinium rings of different layers are shown by orange dashed lines.
of the 9-AA cation. 9-Aminoacidinium 3-chlorobenzoate (AQAGEF; Sikorski & Trzybiński, 2011b) crystallizes in the monoclinic P2_1/c space group with an 9-AA cation and a 3-chlorobenzoate anion in the asymmetric unit and the crystal structure features N—H· · ·O and C—H· · ·O hydrogen bonds and π–π stacking interactions. Inversely oriented cations and anions form a tetramer; these ions are linked via N(amino)—H· · ·O (carboxy) hydrogen bonds, forming a ring motif. 9-Aminoacidinium 3-chlorobenzoate (AQAGUJ; Sikorski & Trzybiński, 2011b) forms triclinic crystals (P̅1 space group) with an 9-AA cation, a 4-chlorobenzoate anion and a water molecule in the asymmetric unit. The crystal structure features N—H· · ·O and O—H· · ·O hydrogen bonds and π–π interactions. Analysis of the hydrogen bonds in the structure of this compound shows that the ions form tetramers and produce an R̅_4^1(16) hydrogen-bond ring motif. 9-Aminoacidinium 3-hydroxybenzoate (AQAGOP; Sikorski & Trzybiński, 2011b) also crystallizes in the triclinic P̅1 space group, the asymmetric unit consisting of two 9-AA cations, 3-hydroxybenzoate and chloride anions as well as two water molecules. This structure is the first of all the known 9-aminoacidinium salts where mixed salts were obtained (Allen, 2002). The average deviations from planarity of the acridine skeleton are 0.015 (2) and 0.027 (2) Å, and the angle between the mean planes of the right- and left-hand halves of the acridine skeleton is 1.5 and 3.7° in cations A and B, respectively. Analysis of the hydrogen bonds in this compound shows that the ions do not form tetramers, but produce two nearly perpendicularly aligned kinds of hydrogen-bonded chain motif. 9-Aminoacidinium chloride methanol solvate (SIDHAQ; Trzybiński & Sikorski, 2013) again forms triclinic crystals (P̅1 space group). The amino group of the 9-aminoacidinium cation interacts with the chloride anion via an N—H· · ·Cl hydrogen bond and the methanol molecule via an N—H· · ·O hydrogen bond, generating a centrosymmetric R̅_4^1(16) supramolecular synthon. The methanol molecule interacts with the halide ion; the resulting supramolecular synthon R̅_4^1(12) is not planar but assumes a chair shape. This hydrogen-bonded ring motif is stabilized by the N—H· · ·Cl hydrogen bond between the acridinium skeleton and the halide ion.

5. Synthesis and crystallization

9-Aminoacidinium hydrochloride (0.0624 g, 2.71 × 10^{-4} mol) was dissolved in N,N-dimethylformamide (4 ml) under heating at 418 K until the 9-AA·HCl had fully dissolved. The solution was left to cool to 280 K. Single crystals were obtained after 2 days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed geometrically and refined as riding, with C—H = 0.93 Å and Uiso(H) = 1.2Ueq(C) for aromatic hydrogens and the C—H group and C—H = 0.96 Å and Uiso(H) = 1.5Ueq(C) for the CH3 group. A rotating model was used for the methyl group.

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### Table 2

| Crystal data                      | Chemical formula | C_{13}H_{11}N_{3}+·Cl−·C_{6}H_{4}NO |
|-----------------------------------|------------------|-------------------------------------|
| Mass (Da)                         |                  | 303.78                              |
| Crystal system, space group       |                  | Monoclinic, P2_1/c                  |
| Temperature (K)                   |                  | 293                                 |
| a, b, c (Å)                       |                  | 10.5819 (7), 42.705 (2), 7.2531 (6) |
| β (°)                             |                  | 108.800 (8)                         |
| V (Å³)                            |                  | 3102.8 (4)                          |
| Z                                 |                  | 8                                   |
| Radiation type                    |                  | Mo Ka                               |
| μ (mm⁻¹)                          |                  | 0.25                                |
| Crystal size (mm)                 |                  | 0.3 × 0.2 × 0.15                    |
| Data collection                   |                  | Xcalibur, Eos                       |
| Absorption correction             |                  | Multi-scan (CrysAlis PRO; Rigaku OD, 2019) |
| Tmin, Tmax                        |                  | 0.955, 1.000                        |
| No. of measured, independent and observed reflections | | 12374, 5491, 3496 |
| Rint                             |                  | 0.040                               |
| (sin θ/λ)max (Å⁻¹)                |                  | 0.595                               |
| Refinement                        |                  | R(F² > 2σ(F²)), wR(F²), S |                  | 0.085, 0.199, 1.10 |
| No. of reflections                |                  | 5491                                |
| No. of parameters                 |                  | 383                                 |
| H-atom treatment                  |                  | H-atom parameters constrained       |
| Δρobs max, Δρcalc max (e Å⁻³)     |                  | 0.58, -0.27                         |

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Computer programs: CrysAlis PRO (Rigaku OD, 2019), SHELXT (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).

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synthon (Etter, 1990; Etter et al., 1990; Aakeröy, 1997). The dimers are also stabilized by C—H· · ·Cl hydrogen bonds between C atoms in positions 1 and 8 in the 9-AA skeleton and the halide ions [d(C—C· · ·Cl) = 3.608 (5)–3.688 (4) Å and C—H· · ·Cl = 163-172°] (Fig. 2), as is also observed in other 9-AA salts (Sikorski & Trzybiński, 2011a,b; 2013).

Adjacent acridine skeletons are linked via π–π stacking interactions in an AB arrangement (Fig. 3). All of the aromatic rings of the A molecules participate in π–π interactions, propagating in zigzag manner along the c-axis direction with centroid–centroid distances ranging from 3.9786 (3) to 4.2236 (3) Å. On the other hand, only the two aromatic rings of the acridine B molecules participate in π–π interactions, with adjacent acridine skeletons rotated in-plane with respect to one another. The centroid–centroid distances vary from 3.6514 (3) to 4.7445 (5) Å.

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4. Database survey

A search of the Cambridge Structure Database (CSD version 5.42, last update February 2021; Groom et al., 2016) revealed that the current structure has never been published before. 101 structures containing 9-AA cations and chloride anions were found. These include 9-aminoacidinium hydrochloride monohydrate (refcode: AMACRD; Talacki et al., 1974), which consists of a monoionized 9-aminoacidine molecule with the proton on the N atom of the central ring, one water molecule, which is hydrogen bonded to another water molecule, and two chloride ions, which are hydrogen bonded to the amino group.
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Crystal structure of 9-aminoacridinium chloride N,N-dimethylformamide monosolvate

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Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2019); cell refinement: CrysAlis PRO (Rigaku OD, 2019); data reduction: CrysAlis PRO (Rigaku OD, 2019); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Crystal data

| C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>Cl·C<sub>3</sub>H<sub>7</sub>NO | F(000) = 1280 |
|---------|------------|
| Mr = 303.78 | D<sub>x</sub> = 1.301 Mg m<sup>-3</sup> |
| Monoclinic, P<sub>2</sub>1/c | Mo Kα radiation, λ = 0.71073 Å |
| a = 10.5819 (7) Å | Cell parameters from 3798 reflections |
| b = 42.705 (2) Å | θ = 2.1–26.7° |
| c = 7.2531 (6) Å | μ = 0.25 mm<sup>-1</sup> |
| β = 108.800 (8)° | T = 293 K |
| V = 3102.8 (4) Å<sup>3</sup> | Block, clear intense yellow |
| Z = 8 | 0.3 × 0.2 × 0.15 mm |

Data collection

| Xcalibur, Eos diffraclometer | 5491 independent reflections |
| Detector resolution: 8.0797 pixels mm<sup>-1</sup> | 3496 reflections with I > 2σ(I) |
| ω scans | R<sub>int</sub> = 0.040 |
| Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019) | θ<sub>max</sub> = 25.0°, θ<sub>min</sub> = 1.9° |
| | h = −8→12 |
| | k = −34→50 |
| | l = −8→8 |
| T<sub>min</sub> = 0.955, T<sub>max</sub> = 1.000 | 12374 measured reflections |

Refinement

| Refinement on F<sup>2</sup> | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.085 | w = 1/[σ<sup>2</sup>(F<sup>2</sup>) + (0.0638P)<sup>2</sup> + 2.1432P] |
| wR(F<sup>2</sup>) = 0.199 | where P = (F<sup>2</sup> + 2F<sup>c</sup>)/3 |
| S = 1.10 | (Δ/σ)max = 0.001 |
| 5491 reflections | Δρ<sub>max</sub> = 0.58 e Å<sup>-3</sup> |
| 383 parameters | Δρ<sub>min</sub> = −0.27 e Å<sup>-3</sup> |
| 0 restraints |
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)

|       | x     | y     | z     | Ueq  |
|-------|-------|-------|-------|------|
| Cl2   | 0.52995 (11) | 0.60004 (2) | 0.42541 (19) | 0.0646 (4) |
| Cl1   | 0.92064 (11)  | 0.65087 (2)  | 0.79353 (19)  | 0.0652 (4)  |
| N2    | 0.4780 (3)    | 0.75521 (8)  | 0.2516 (5)    | 0.0473 (9)  |
| H2    | 0.439961      | 0.772953     | 0.214055      | 0.057*      |
| N4    | 0.8349 (3)    | 0.58046 (8)  | 0.6530 (5)    | 0.0558 (10) |
| H4A   | 0.753411      | 0.581081     | 0.577485      | 0.067*      |
| H4B   | 0.875157      | 0.597465     | 0.702537      | 0.067*      |
| N1    | 0.6495 (3)    | 0.67060 (8)  | 0.4611 (5)    | 0.0546 (10) |
| H1A   | 0.729108      | 0.669943     | 0.542722      | 0.066*      |
| H1B   | 0.604150      | 0.653625     | 0.427738      | 0.066*      |
| N5    | 1.0324 (4)    | 0.49648 (8)  | 0.7759 (5)    | 0.0572 (10) |
| H5A   | 1.074306      | 0.478926     | 0.801115      | 0.069*      |
| N3    | 0.1963 (4)    | 0.84737 (8)  | −0.0005 (6)   | 0.0591 (10) |
| N6    | 1.3057 (4)    | 0.40331 (10) | 0.9714 (6)    | 0.0646 (11) |
| C2    | 0.6704 (4)    | 0.72613 (9)  | 0.4405 (6)    | 0.0407 (10) |
| C7    | 0.6074 (4)    | 0.75488 (9)  | 0.3723 (6)    | 0.0419 (10) |
| C29   | 0.8324 (4)    | 0.52493 (9)  | 0.6113 (6)    | 0.0441 (10) |
| C1    | 0.5973 (4)    | 0.69747 (9)  | 0.3876 (6)    | 0.0411 (10) |
| C13   | 0.4638 (4)    | 0.69898 (9)  | 0.2499 (6)    | 0.0415 (10) |
| C17   | 0.8978 (4)    | 0.55533 (9)  | 0.6925 (6)    | 0.0433 (10) |
| C8    | 0.4070 (4)    | 0.72836 (9)  | 0.1884 (6)    | 0.0427 (10) |
| C18   | 1.0344 (4)    | 0.55202 (10) | 0.8188 (6)    | 0.0469 (10) |
| C12   | 0.3863 (4)    | 0.67215 (10) | 0.1781 (6)    | 0.0502 (11) |
| H12   | 0.421945      | 0.652389     | 0.216721      | 0.060*      |
| C3    | 0.8063 (4)    | 0.72726 (10) | 0.5627 (6)    | 0.0478 (11) |
| H3    | 0.851443      | 0.708777     | 0.610598      | 0.057*      |
| C23   | 1.0976 (4)    | 0.52306 (10) | 0.8578 (6)    | 0.0486 (11) |
| C11   | 0.2594 (4)    | 0.67488 (11) | 0.0522 (6)    | 0.0575 (12) |
| H11   | 0.209574      | 0.656968     | 0.004566      | 0.069*      |
| C6    | 0.6752 (5)    | 0.78324 (10) | 0.4249 (6)    | 0.0533 (12) |
| H6    | 0.631891      | 0.802055     | 0.380356      | 0.064*      |
| C24   | 0.9034 (5)    | 0.49659 (10) | 0.6557 (6)    | 0.0496 (11) |
| O1    | 0.3482 (5)    | 0.81000 (10) | 0.1214 (7)    | 0.1213 (17) |
| C19   | 1.1073 (4)    | 0.57874 (11) | 0.9076 (7)    | 0.0578 (12) |
| H19   | 1.067290      | 0.598375     | 0.884741      | 0.069*      |
| C28   | 0.6990 (4)    | 0.52341 (10) | 0.4876 (7)    | 0.0593 (12) |
| H28   | 0.649844      | 0.541808     | 0.454043      | 0.071*      |
| C9    | 0.2745 (4)    | 0.75091 (11) | 0.0596 (7)    | 0.0575 (12) |
| H9    | 0.236582      | 0.750446     | 0.020291      | 0.069*      |
Atomic displacement parameters (Å²)

| Atom | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|------|------|------|------|------|------|------|
| C4   | 0.8703 (4) | 0.75517 (10) | 0.6096 (6) | 0.0559 (12) |
| H4   | 0.959115 | 0.755529 | 0.688614 | 0.067* |
| C5   | 0.8052 (5) | 0.78322 (11) | 0.5416 (6) | 0.0595 (13) |
| H5   | 0.850566 | 0.802089 | 0.575935 | 0.071* |
| C22  | 1.2312 (5) | 0.52056 (12) | 0.9817 (7) | 0.0634 (13) |
| H22  | 1.273053 | 0.501138 | 1.006910 | 0.076* |
| C10  | 0.2037 (5) | 0.70426 (11) | −0.0055 (7) | 0.0625 (13) |
| H10  | 0.116652 | 0.705698 | −0.089990 | 0.075* |
| C25  | 0.8413 (5) | 0.46818 (11) | 0.5788 (7) | 0.0640 (13) |
| H25  | 0.889114 | 0.449551 | 0.608286 | 0.077* |
| C21  | 1.2971 (5) | 0.54672 (12) | 1.0626 (7) | 0.0657 (14) |
| H21  | 1.384991 | 0.545175 | 1.144215 | 0.079* |
| C20  | 1.2366 (5) | 0.57594 (12) | 1.0269 (7) | 0.0649 (13) |
| H20  | 1.284081 | 0.593680 | 1.084266 | 0.078* |
| C14  | 0.3158 (6) | 0.83691 (14) | 0.0906 (8) | 0.0750 (15) |
| C16  | 0.382748 | 0.851803 | 0.136486 | 0.090* |
| C26  | 0.7123 (5) | 0.46777 (11) | 0.4620 (7) | 0.0709 (15) |
| H26  | 0.671583 | 0.448903 | 0.412320 | 0.085* |
| C27  | 0.6406 (5) | 0.49580 (12) | 0.4165 (7) | 0.0689 (14) |
| H27  | 0.552007 | 0.495458 | 0.336611 | 0.083* |
| O2   | 1.1518 (6) | 0.43877 (11) | 0.8412 (8) | 0.149 (2) |
| C16  | 0.1695 (6) | 0.88039 (13) | −0.0371 (11) | 0.115 (2) |
| H16A | 0.248518 | 0.892193 | 0.028244 | 0.172* |
| H16B | 0.098683 | 0.886614 | 0.010836 | 0.172* |
| C14  | 0.143641 | 0.884297 | −0.174604 | 0.172* |
| C32  | 1.3588 (7) | 0.37299 (14) | 1.0227 (10) | 0.121 (3) |
| H32A | 1.371578 | 0.369283 | 1.158012 | 0.181* |
| H32B | 1.442925 | 0.371355 | 0.999575 | 0.181* |
| C30  | 1.1894 (8) | 0.4107 (2) | 0.8729 (11) | 0.127 (3) |
| H30  | 1.127945 | 0.394876 | 0.820824 | 0.152* |
| C15  | 0.0865 (6) | 0.82581 (15) | −0.0790 (11) | 0.120 (3) |
| H15A | 0.056623 | 0.826913 | −0.218681 | 0.180* |
| H15B | 0.014377 | 0.831333 | −0.032063 | 0.180* |
| C1    | 1.3999 (9) | 0.42835 (19) | 1.0510 (12) | 0.158 (3) |
| H31A | 1.449884 | 0.423680 | 1.183929 | 0.237* |
| H31B | 1.352309 | 0.447662 | 1.045383 | 0.237* |
| H31C | 1.459666 | 0.430308 | 0.976317 | 0.237* |

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Geometric parameters (Å, º)

| Bond/Angle | Distance/Angle |
|------------|----------------|
| N2—H2      | 0.8600         |
| N2—C7      | 1.367 (5)      |
| N2—C8      | 1.367 (5)      |
| N4—H4A     | 0.8600         |
| N4—H4B     | 0.8600         |
| N4—C17     | 1.313 (5)      |
| N1—H1A     | 0.8600         |
| N1—H1B     | 0.8600         |
| C6—H6      | 0.9300         |
| C6—C5      | 1.363 (6)      |
| C24—C25    | 1.407 (6)      |
| O1—C14     | 1.199 (6)      |
| C19—H19    | 0.999 (6)      |
| C19—C20    | 1.368 (6)      |
| C28—H28    | 0.9300         |
| C28—C27    | 1.354 (6)      |

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| Bond  | Length (Å) | Bond  | Length (Å) | Angle (°) |
|-------|------------|-------|------------|-----------|
| C1—N1 | 1.310 (5)  | C9—H9 | 0.9300     |           |
| C1—N5  | 0.8600     | C10—C9 | 1.361 (6)  |           |
| C1—N5  | 1.361 (5)  | C4—H4 | 0.9300     |           |
| C1—N5  | 1.362 (5)  | C5—C4 | 1.391 (6)  |           |
| C1—N3  | 1.303 (6)  | C5—H5 | 0.9300     |           |
| C1—N3  | 1.446 (6)  | C6—C5 | 1.355 (7)  |           |
| C1—N6  | 1.448 (6)  | C22—C21 | 1.347 (6)  |           |
| C1—N6  | 1.413 (6)  | C10—H10 | 0.9300 |           |
| C1—N6  | 1.248 (7)  | C25—H25 | 0.9300 |           |
| C1—N6  | 1.449 (7)  | C25—C26 | 1.355 (7)  |           |
| C2—C6  | 1.397 (5)  | C21—C20 | 1.388 (6)  |           |
| C2—C2  | 1.405 (5)  | C21—C20 | 1.388 (6)  |           |
| C3—C2  | 1.410 (6)  | C27—H27 | 0.9300 |           |
| C3—C2  | 1.445 (5)  | O2—C30 | 1.260 (8)  |           |
| C4—C1  | 1.401 (5)  | C16—C16A | 0.9600 |           |
| C4—C1  | 1.408 (5)  | C16—H16B | 0.9600 |           |
| C4—C1  | 1.441 (5)  | C16—H16C | 0.9600 |           |
| C5—C4  | 1.391 (5)  | C32—H32A | 0.9600 |           |
| C5—C4  | 1.412 (6)  | C32—H32A | 0.9600 |           |
| C5—C1  | 0.9300     | C30—H30 | 0.9300     |           |
| C6—C5  | 0.9300     | C15—H15A | 0.9600 |           |
| C6—C5  | 1.359 (5)  | C15—H15B | 0.9600 |           |
| C6—C5  | 1.364 (6)  | C31—C31A | 0.9600 |           |
| C6—C5  | 1.290 (6)  | C31—H31B | 0.9600 |           |
| C6—C5  | 1.381 (6)  | C31—H31C | 0.9600 |           |

Other bond angles and distances are as follows:
- C7—N2—H2: 118.8
- C7—N2—C8: 122.3 (3)
- C8—N2—H2: 118.8
- H4A—N4—H4B: 120.0
- C17—N4—H4A: 120.0
- C17—N4—H4B: 120.0
- H1A—N1—H1B: 120.0
- C1—N1—H1A: 120.0
- C1—N1—H1B: 120.0
- C23—N5—H5A: 118.7
- C23—N5—C24: 122.6 (4)
- C24—N5—H5A: 118.7
- C14—N3—C16: 121.9 (5)
- C14—N3—C15: 120.4 (5)
- C16—N3—C15: 117.6 (5)
- C32—N6—C31: 114.0 (6)

Other angles are as follows:
- C7—N2—H2: 118.8
- C7—N2—C8: 122.3 (3)
- C8—N2—H2: 118.8
- H4A—N4—H4B: 120.0
- C17—N4—H4A: 120.0
- C17—N4—H4B: 120.0
- H1A—N1—H1B: 120.0
- C1—N1—H1A: 120.0
- C1—N1—H1B: 120.0
- C23—N5—H5A: 118.7
- C23—N5—C24: 122.6 (4)
- C24—N5—H5A: 118.7
- C14—N3—C16: 121.9 (5)
- C14—N3—C15: 120.4 (5)
- C16—N3—C15: 117.6 (5)
- C32—N6—C31: 114.0 (6)
| Bond          | Distance (Å) | Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|---------------|--------------|
| C30—N6—C32   | 128.2 (6)    | C9—C10—C11   | 121.2 (4)    | C2—C1—C13    | 121.2 (4)    |
| C30—N6—C31   | 117.7 (6)    | C9—C10—H10   | 119.4        | C2—C1—C13    | 120.7 (4)    |
| C7—C2—C1     | 119.8 (3)    | C24—C25—H25  | 119.8        | C8—C13—C1    | 118.0 (3)    |
| C7—C2—C3     | 117.2 (3)    | C24—C25—C24  | 120.5 (4)    | C8—C13—C12   | 118.9 (4)    |
| C3—C2—C1     | 123.0 (4)    | C26—C25—C24  | 119.8        | C12—C13—C1   | 122.9 (4)    |
| N2—C7—C6     | 119.8 (4)    | C26—C25—H25  | 119.3        | C12—C13—C1   | 120.8 (4)    |
| N2—C7—C2     | 119.1 (4)    | C22—C21—C20  | 121.4 (4)    | N4—C17—C29   | 119.2 (4)    |
| C6—C7—C2     | 121.1 (4)    | C22—C21—H21  | 119.3        | N4—C17—C18   | 118.4 (4)    |
| C24—C29—C17  | 119.2 (4)    | C19—C20—C21  | 120.2 (5)    | N2—C8—C13    | 120.8 (4)    |
| C24—C29—C28  | 117.3 (4)    | C19—C20—H20  | 119.9        | N2—C8—C9     | 118.5 (4)    |
| C28—C29—C17  | 123.6 (4)    | C21—C20—H20  | 119.9        | C13—C8—C9    | 120.7 (4)    |
| N1—C1—C2     | 121.2 (4)    | N3—C14—H14   | 116.7        | C23—C18—C17  | 119.2 (4)    |
| N1—C1—C13    | 120.7 (4)    | O1—C14—N3    | 126.6 (6)    | C23—C18—C19  | 118.0 (4)    |
| C2—C1—C13    | 118.0 (3)    | O1—C14—H14   | 116.7        | C19—C18—C17  | 118.2 (4)    |
| C8—C13—C1    | 118.9 (4)    | C25—C26—H26  | 120.1        | C19—C18—C17  | 122.8 (4)    |
| C8—C13—C12   | 118.2 (4)    | C25—C26—C27  | 119.8 (5)    | C13—C12—H12  | 119.7        |
| C12—C13—C1   | 122.9 (4)    | C27—C26—H26  | 120.1        | C11—C12—C13  | 120.6 (4)    |
| N4—C17—C29   | 120.8 (4)    | C28—C27—H27  | 119.7        | C11—C12—H12  | 119.7        |
| N4—C17—C18   | 118.4 (4)    | C26—C27—H27  | 119.7        | C2—C3—H3     | 119.8        |
| N2—C8—C13    | 120.8 (3)    | N3—C16—H16A  | 109.5        | C4—C3—C2     | 120.4 (4)    |
| N2—C8—C9     | 118.5 (4)    | N3—C16—H16B  | 109.5        | C4—C3—H3     | 119.8        |
| C13—C8—C9    | 120.7 (4)    | N3—C16—H16C  | 109.5        | N5—C23—C18   | 120.6 (4)    |
| C23—C18—C17  | 119.2 (4)    | H16A—C16—H16B| 109.5        | N5—C23—C22   | 118.5 (4)    |
| C23—C18—C19  | 118.0 (4)    | H16A—C16—H16C| 109.5        | C18—C23—C22  | 120.9 (4)    |
| C19—C18—C17  | 122.8 (4)    | H16B—C16—H16C| 109.5        | C12—C11—H11  | 119.7        |
| C13—C12—H12  | 119.7        | N6—C32—H32A  | 109.5        | C12—C11—C10  | 120.5 (4)    |
| C11—C12—C13  | 120.6 (4)    | N6—C32—H32B  | 109.5        | C10—C11—H11  | 119.7        |
| C11—C12—H12  | 119.7        | N6—C32—H32C  | 109.5        | C7—C6—H6     | 120.1        |
| C2—C3—H3     | 119.8        | H32B—C32—H32C| 109.5        | C5—C6—C7     | 119.8 (4)    |
| C4—C3—C2     | 120.4 (4)    | H32B—C32—H32C| 109.5        | C5—C6—H6     | 120.1        |
| C4—C3—H3     | 119.8        | H32B—C32—H32C| 109.5        | N5—C24—C29   | 120.0 (4)    |
| N5—C23—C18   | 120.6 (4)    | N6—C30—O2    | 122.7 (8)    | N5—C24—C25   | 119.7 (4)    |
| N5—C23—C22   | 118.5 (4)    | N6—C30—H30   | 118.6        | C29—C24—C25  | 120.3 (4)    |
| C18—C19—H19  | 119.8        | O2—C30—H30   | 118.6        | C18—C19—H19  | 119.8        |
| C20—C19—C18  | 120.4 (4)    | N6—C31—H31B  | 109.5        | C20—C19—C18  | 119.8        |
| C20—C19—H19  | 119.8        | N6—C31—H31C  | 109.5        |
### Supporting Information

#### Hydrogen-bond geometry (Å, °)

| D—H···A         | D—H | H···A | D···A   | D—H···A |
|-----------------|-----|-------|---------|---------|
| N2—H2···O1      | 0.86| 1.86  | 2.723 (5)| 176     |
| N4—H4A···Cl2    | 0.86| 2.40  | 3.225 (3)| 160     |
| N4—H4B···Cl1    | 0.86| 2.38  | 3.211 (4)| 163     |
| N1—H1A···Cl1    | 0.86| 2.39  | 3.209 (3)| 160     |
| N1—H1B···Cl2    | 0.86| 2.42  | 3.246 (3)| 162     |
| N5—H5A···O2     | 0.86| 1.88  | 2.740 (5)| 175     |