



Crystal structure of 9-aminoacridinium chloride *N,N*-dimethylformamide monosolvate

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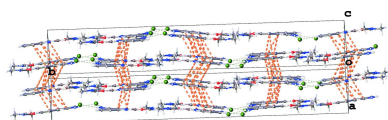
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9-Aminoacridinium chloride *N,N*-dimethylformamide monosolvate, $C_{13}H_{11}N_2^+Cl^- \cdot C_3H_7NO$, crystallizes in the monoclinic space group $P2_1/c$. The salt was crystallized from *N,N*-dimethylformamide. The asymmetric unit consists of two $C_{13}H_{11}N_2^+Cl^-$ 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 π - π interactions between the 9-AA rings, and the whole lattice is additionally stabilized by electrostatic interactions between ions.

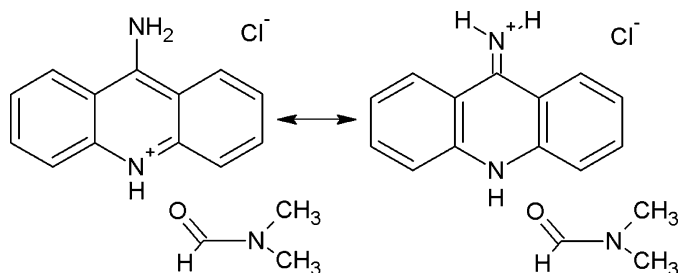
1. Chemical context

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 guanidinobenzoates (GB) (Murza *et al.*, 2000). Interestingly, cellulose nanocomposites based on $[Fe(hptrz)_3](OTs)_2$ nanoparticles were effectively doped with 9-AA, resulting in a thermochromic and thermofluorescent 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 *N,N*-dimethylformamide solvate (1:1).



2. Structural commentary

The title compound crystallizes in the monoclinic $P2_1/c$ space group, with two 9-AA⁺Cl⁻ 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–NH₂ bonds C1–N1 and C17–N4 are 1.310 (5) and 1.313 (5) Å, respectively. These bond lengths are characteristic for a C=N 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.

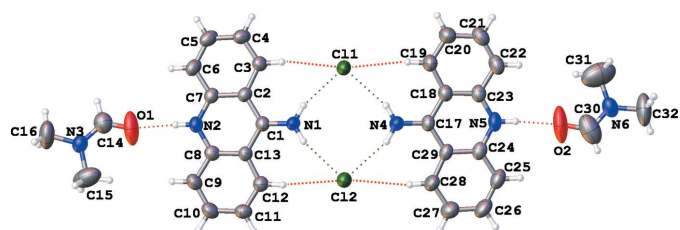


Figure 1

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 $R_2^2(8)$ synthon.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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

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 π – π stacking interactions. The 9-AA molecules form layers (Fig. 3), which stack perpendicularly to the 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 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 H5A, attached to N2 and N5, form hydrogen bonds to *N,N*-dimethylformamide atoms, O1 and O2, with $d(N\cdots O) = 2.723(5)$ – $2.740(5)$ Å, $N-H\cdots O = 175$ – 176° . The chloride ions are linked *via* N–H···Cl hydrogen bonds [$d(N\cdots Cl) = 3.209(3)$ – $3.246(3)$ Å, $N-H\cdots Cl = 160$ – 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 $R_2^2(8)$ supramolecular

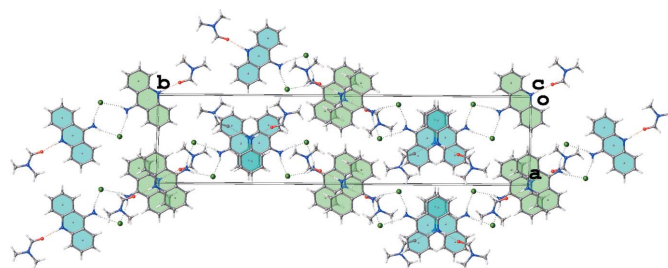


Figure 2

Crystal packing viewed along the c axis. The N–H···Cl and N–H···O interactions are represented by green and red dashed lines, respectively. The *A* and *B* acridine molecules are coloured green and blue, respectively.

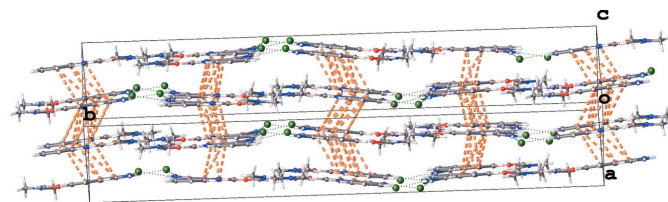


Figure 3

Layers of 9-AA. π – π stacking interactions between the 9-aminoacridinium rings of different layers are shown by orange dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{11}N_2^+ \cdot Cl^- \cdot C_3H_7NO$
M_r	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 (Å ³)	3102.8 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.25
Crystal size (mm)	0.3 × 0.2 × 0.15
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2019)
T_{\min} , T_{\max}	0.955, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12374, 5491, 3496
R_{int}	0.040
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.085, 0.199, 1.10
No. of reflections	5491
No. of parameters	383
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.58, -0.27

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

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 [$d(C \cdots Cl) = 3.608$ (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.

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-aminoacridine hydrochloride monohydrate (refcode: AMACRD; Talacki *et al.*, 1974), which consists of a monoionized 9-aminoacridine 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

of the 9-AA cation. 9-Aminoacridinium 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-Aminoacridinium 3-chlorobenzoate (AQAGIJ; (Sikorski & Trzybiński, 2011b) forms triclinic crystals ($P\bar{1}$ 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 compounds shows that the ions form tetramers and produce an $R_2^4(16)$ hydrogen-bond ring motif. 9-Aminoacridinium 3-hydroxybenzoate (AQAGOP; Sikorski & Trzybiński, 2011b) also crystallizes in the triclinic $P\bar{1}$ space group, the asymmetric unit consisting of two 9-AA cations, 3-hydroxybenzoate and chlorate anions as well as two water molecules. This structure is the first of all the known 9-aminoacridinium 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-Aminoacridinium chloride methanol solvate (SIDHAQ; Trzybiński & Sikorski, 2013) again forms triclinic crystals ($P\bar{1}$ space group). The amino group of the 9-aminoacridinium 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 $R_2^4(16)$ supramolecular synthon. The methanol molecule interacts with the halide ion; the resulting supramolecular synthon $R_2^4(12)$ 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-Aminoacridinium 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic hydrogens and the C—H group and C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the CH₃ group. A rotating model was used for the methyl group.

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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).

9-Aminoacridinium chloride *N,N*-dimethylformamide monosolvate

Crystal data

$C_{13}H_{11}N_2^+ \cdot Cl^- \cdot C_3H_7NO$
 $M_r = 303.78$
 Monoclinic, $P2_1/c$
 $a = 10.5819$ (7) Å
 $b = 42.705$ (2) Å
 $c = 7.2531$ (6) Å
 $\beta = 108.800$ (8)°
 $V = 3102.8$ (4) Å³
 $Z = 8$

$F(000) = 1280$
 $D_x = 1.301$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3798 reflections
 $\theta = 2.1$ – 26.7 °
 $\mu = 0.25$ mm⁻¹
 $T = 293$ K
 Block, clear intense yellow
 $0.3 \times 0.2 \times 0.15$ mm

Data collection

Xcalibur, Eos
 diffractometer
 Detector resolution: 8.0797 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2019)
 $T_{\min} = 0.955$, $T_{\max} = 1.000$
 12374 measured reflections

5491 independent reflections
 3496 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\max} = 25.0$ °, $\theta_{\min} = 1.9$ °
 $h = -8 \rightarrow 12$
 $k = -34 \rightarrow 50$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.085$
 $wR(F^2) = 0.199$
 $S = 1.10$
 5491 reflections
 383 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 2.1432P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.58$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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)	0.55353 (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)	0.73091 (11)	0.0596 (7)	0.0575 (12)
H9	0.236582	0.750446	0.020291	0.069*

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)
H14	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*
H16C	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*
H32C	1.297962	0.357724	0.945223	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*
H15C	0.115624	0.804886	-0.038441	0.180*
C31	1.3999 (9)	0.42835 (19)	1.0510 (12)	0.158 (3)
H31A	1.449984	0.423680	1.183929	0.237*
H31B	1.352309	0.447662	1.045383	0.237*
H31C	1.459666	0.430308	0.976317	0.237*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.0509 (7)	0.0407 (6)	0.0845 (9)	0.0001 (5)	-0.0026 (6)	0.0013 (6)
Cl1	0.0487 (7)	0.0370 (6)	0.0911 (9)	0.0017 (5)	-0.0038 (6)	-0.0027 (6)
N2	0.049 (2)	0.039 (2)	0.050 (2)	0.0050 (16)	0.0093 (17)	0.0074 (17)
N4	0.043 (2)	0.039 (2)	0.075 (3)	0.0002 (16)	0.0048 (18)	-0.0053 (19)
N1	0.044 (2)	0.0325 (19)	0.073 (3)	-0.0036 (15)	-0.0020 (18)	0.0044 (18)

N5	0.065 (3)	0.042 (2)	0.061 (3)	0.0161 (19)	0.017 (2)	0.0092 (19)
N3	0.058 (2)	0.044 (2)	0.074 (3)	0.0020 (19)	0.020 (2)	0.004 (2)
N6	0.054 (2)	0.064 (3)	0.077 (3)	0.012 (2)	0.023 (2)	0.014 (2)
C2	0.046 (2)	0.035 (2)	0.040 (2)	-0.0028 (18)	0.0128 (19)	0.0019 (19)
C7	0.049 (2)	0.038 (2)	0.038 (2)	-0.0003 (19)	0.014 (2)	0.0001 (19)
C29	0.054 (3)	0.033 (2)	0.048 (3)	0.0019 (19)	0.021 (2)	0.000 (2)
C1	0.042 (2)	0.039 (2)	0.041 (2)	0.0038 (18)	0.0114 (18)	-0.0004 (19)
C13	0.042 (2)	0.037 (2)	0.043 (2)	0.0002 (18)	0.0107 (18)	0.0056 (19)
C17	0.048 (2)	0.038 (2)	0.045 (2)	0.0074 (19)	0.0157 (19)	0.000 (2)
C8	0.043 (2)	0.046 (3)	0.038 (2)	-0.0017 (19)	0.0116 (18)	0.005 (2)
C18	0.048 (2)	0.045 (3)	0.048 (3)	0.007 (2)	0.014 (2)	0.002 (2)
C12	0.049 (3)	0.045 (3)	0.052 (3)	0.000 (2)	0.010 (2)	0.003 (2)
C3	0.045 (2)	0.043 (3)	0.048 (3)	0.0000 (19)	0.005 (2)	0.004 (2)
C23	0.055 (3)	0.046 (3)	0.045 (3)	0.008 (2)	0.016 (2)	0.004 (2)
C11	0.046 (3)	0.055 (3)	0.063 (3)	-0.008 (2)	0.004 (2)	-0.001 (2)
C6	0.070 (3)	0.036 (2)	0.049 (3)	-0.005 (2)	0.012 (2)	0.004 (2)
C24	0.065 (3)	0.040 (3)	0.048 (3)	0.004 (2)	0.023 (2)	0.002 (2)
O1	0.159 (4)	0.091 (3)	0.131 (4)	0.074 (3)	0.070 (3)	0.058 (3)
C19	0.052 (3)	0.046 (3)	0.069 (3)	0.007 (2)	0.011 (2)	-0.004 (2)
C28	0.059 (3)	0.041 (3)	0.071 (3)	0.000 (2)	0.011 (2)	-0.009 (2)
C9	0.045 (3)	0.056 (3)	0.062 (3)	0.005 (2)	0.004 (2)	0.010 (2)
C4	0.055 (3)	0.050 (3)	0.052 (3)	-0.013 (2)	0.002 (2)	0.005 (2)
C5	0.075 (3)	0.045 (3)	0.051 (3)	-0.016 (2)	0.010 (2)	0.000 (2)
C22	0.058 (3)	0.066 (3)	0.063 (3)	0.022 (3)	0.015 (2)	0.005 (3)
C10	0.048 (3)	0.063 (3)	0.063 (3)	0.001 (2)	-0.001 (2)	0.012 (3)
C25	0.088 (4)	0.038 (3)	0.066 (3)	0.005 (2)	0.024 (3)	-0.002 (2)
C21	0.050 (3)	0.074 (4)	0.064 (3)	0.013 (3)	0.006 (2)	0.008 (3)
C20	0.054 (3)	0.059 (3)	0.070 (3)	0.001 (2)	0.004 (2)	-0.004 (3)
C14	0.077 (4)	0.073 (4)	0.074 (4)	0.009 (3)	0.023 (3)	0.007 (3)
C26	0.092 (4)	0.043 (3)	0.073 (4)	-0.007 (3)	0.019 (3)	-0.013 (3)
C27	0.066 (3)	0.060 (3)	0.074 (3)	-0.004 (3)	0.012 (3)	-0.014 (3)
O2	0.183 (5)	0.100 (4)	0.181 (5)	0.093 (4)	0.082 (4)	0.065 (4)
C16	0.119 (5)	0.063 (4)	0.169 (7)	0.036 (4)	0.056 (5)	0.030 (4)
C32	0.160 (7)	0.084 (5)	0.126 (6)	0.069 (4)	0.060 (5)	0.032 (4)
C30	0.111 (6)	0.147 (7)	0.122 (6)	0.048 (5)	0.039 (5)	0.044 (5)
C15	0.102 (5)	0.108 (5)	0.157 (7)	-0.042 (4)	0.051 (5)	-0.040 (5)
C31	0.180 (8)	0.153 (8)	0.142 (7)	-0.073 (7)	0.053 (6)	-0.008 (6)

Geometric parameters (Å, °)

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

N1—C1	1.310 (5)	C9—H9	0.9300
N5—H5A	0.8600	C9—C10	1.361 (6)
N5—C23	1.361 (5)	C4—H4	0.9300
N5—C24	1.362 (5)	C4—C5	1.391 (6)
N3—C14	1.303 (6)	C5—H5	0.9300
N3—C16	1.446 (6)	C22—H22	0.9300
N3—C15	1.448 (6)	C22—C21	1.347 (6)
N6—C32	1.413 (6)	C10—H10	0.9300
N6—C30	1.248 (7)	C25—H25	0.9300
N6—C31	1.449 (7)	C25—C26	1.355 (7)
C2—C7	1.409 (5)	C21—H21	0.9300
C2—C1	1.433 (5)	C21—C20	1.388 (6)
C2—C3	1.426 (5)	C20—H20	0.9300
C7—C6	1.397 (5)	C14—H14	0.9300
C29—C17	1.434 (5)	C26—H26	0.9300
C29—C24	1.406 (5)	C26—C27	1.399 (6)
C29—C28	1.410 (6)	C27—H27	0.9300
C1—C13	1.445 (5)	O2—C30	1.260 (8)
C13—C8	1.401 (5)	C16—H16A	0.9600
C13—C12	1.408 (5)	C16—H16B	0.9600
C17—C18	1.441 (5)	C16—H16C	0.9600
C8—C9	1.416 (5)	C32—H32A	0.9600
C18—C23	1.391 (5)	C32—H32B	0.9600
C18—C19	1.412 (6)	C32—H32C	0.9600
C12—H12	0.9300	C30—H30	0.9300
C12—C11	1.364 (6)	C15—H15A	0.9600
C3—H3	0.9300	C15—H15B	0.9600
C3—C4	1.359 (5)	C15—H15C	0.9600
C23—C22	1.414 (6)	C31—H31A	0.9600
C11—H11	0.9300	C31—H31B	0.9600
C11—C10	1.391 (6)	C31—H31C	0.9600
C7—N2—H2	118.8	C29—C28—H28	119.2
C7—N2—C8	122.3 (3)	C27—C28—C29	121.5 (4)
C8—N2—H2	118.8	C27—C28—H28	119.2
H4A—N4—H4B	120.0	C8—C9—H9	120.6
C17—N4—H4A	120.0	C10—C9—C8	118.8 (4)
C17—N4—H4B	120.0	C10—C9—H9	120.6
H1A—N1—H1B	120.0	C3—C4—H4	119.4
C1—N1—H1A	120.0	C3—C4—C5	121.1 (4)
C1—N1—H1B	120.0	C5—C4—H4	119.4
C23—N5—H5A	118.7	C6—C5—C4	120.4 (4)
C23—N5—C24	122.6 (4)	C6—C5—H5	119.8
C24—N5—H5A	118.7	C4—C5—H5	119.8
C14—N3—C16	121.9 (5)	C23—C22—H22	120.5
C14—N3—C15	120.4 (5)	C21—C22—C23	119.0 (4)
C16—N3—C15	117.6 (5)	C21—C22—H22	120.5
C32—N6—C31	114.0 (6)	C11—C10—H10	119.4

C30—N6—C32	128.2 (6)	C9—C10—C11	121.2 (4)
C30—N6—C31	117.7 (6)	C9—C10—H10	119.4
C7—C2—C1	119.8 (3)	C24—C25—H25	119.8
C7—C2—C3	117.2 (3)	C26—C25—C24	120.5 (4)
C3—C2—C1	123.0 (4)	C26—C25—H25	119.8
N2—C7—C2	119.8 (4)	C22—C21—H21	119.3
N2—C7—C6	119.1 (4)	C22—C21—C20	121.4 (4)
C6—C7—C2	121.1 (4)	C20—C21—H21	119.3
C24—C29—C17	119.2 (4)	C19—C20—C21	120.2 (5)
C24—C29—C28	117.3 (4)	C19—C20—H20	119.9
C28—C29—C17	123.6 (4)	C21—C20—H20	119.9
N1—C1—C2	121.2 (4)	N3—C14—H14	116.7
N1—C1—C13	120.7 (4)	O1—C14—N3	126.6 (6)
C2—C1—C13	118.0 (3)	O1—C14—H14	116.7
C8—C13—C1	118.9 (4)	C25—C26—H26	120.1
C8—C13—C12	118.2 (4)	C25—C26—C27	119.8 (5)
C12—C13—C1	122.9 (4)	C27—C26—H26	120.1
N4—C17—C29	120.8 (4)	C28—C27—C26	120.6 (5)
N4—C17—C18	120.8 (4)	C28—C27—H27	119.7
C29—C17—C18	118.4 (4)	C26—C27—H27	119.7
N2—C8—C13	120.8 (3)	N3—C16—H16A	109.5
N2—C8—C9	118.5 (4)	N3—C16—H16B	109.5
C13—C8—C9	120.7 (4)	N3—C16—H16C	109.5
C23—C18—C17	119.2 (4)	H16A—C16—H16B	109.5
C23—C18—C19	118.0 (4)	H16A—C16—H16C	109.5
C19—C18—C17	122.8 (4)	H16B—C16—H16C	109.5
C13—C12—H12	119.7	N6—C32—H32A	109.5
C11—C12—C13	120.6 (4)	N6—C32—H32B	109.5
C11—C12—H12	119.7	N6—C32—H32C	109.5
C2—C3—H3	119.8	H32A—C32—H32B	109.5
C4—C3—C2	120.4 (4)	H32A—C32—H32C	109.5
C4—C3—H3	119.8	H32B—C32—H32C	109.5
N5—C23—C18	120.6 (4)	N6—C30—O2	122.7 (8)
N5—C23—C22	118.5 (4)	N6—C30—H30	118.6
C18—C23—C22	120.9 (4)	O2—C30—H30	118.6
C12—C11—H11	119.7	N3—C15—H15A	109.5
C12—C11—C10	120.5 (4)	N3—C15—H15B	109.5
C10—C11—H11	119.7	N3—C15—H15C	109.5
C7—C6—H6	120.1	H15A—C15—H15B	109.5
C5—C6—C7	119.8 (4)	H15A—C15—H15C	109.5
C5—C6—H6	120.1	H15B—C15—H15C	109.5
N5—C24—C29	120.0 (4)	N6—C31—H31A	109.5
N5—C24—C25	119.7 (4)	N6—C31—H31B	109.5
C29—C24—C25	120.3 (4)	N6—C31—H31C	109.5
C18—C19—H19	119.8	H31A—C31—H31B	109.5
C20—C19—C18	120.4 (4)	H31A—C31—H31C	109.5
C20—C19—H19	119.8	H31B—C31—H31C	109.5

N2—C7—C6—C5	-178.5 (4)	C8—N2—C7—C2	-1.9 (6)
N2—C8—C9—C10	179.3 (4)	C8—N2—C7—C6	177.6 (4)
N4—C17—C18—C23	179.8 (4)	C8—C13—C12—C11	-0.1 (6)
N4—C17—C18—C19	0.5 (7)	C8—C9—C10—C11	0.0 (7)
N1—C1—C13—C8	174.2 (4)	C18—C23—C22—C21	0.1 (7)
N1—C1—C13—C12	-4.1 (6)	C18—C19—C20—C21	-0.3 (7)
N5—C23—C22—C21	179.6 (4)	C12—C13—C8—N2	-179.3 (4)
N5—C24—C25—C26	178.7 (4)	C12—C13—C8—C9	0.9 (6)
C2—C7—C6—C5	1.0 (7)	C12—C11—C10—C9	0.8 (8)
C2—C1—C13—C8	-6.0 (6)	C3—C2—C7—N2	178.7 (4)
C2—C1—C13—C12	175.7 (4)	C3—C2—C7—C6	-0.8 (6)
C2—C3—C4—C5	0.5 (7)	C3—C2—C1—N1	4.9 (6)
C7—N2—C8—C13	1.7 (6)	C3—C2—C1—C13	-174.9 (4)
C7—N2—C8—C9	-178.5 (4)	C3—C4—C5—C6	-0.3 (7)
C7—C2—C1—N1	-174.4 (4)	C23—N5—C24—C29	0.2 (6)
C7—C2—C1—C13	5.8 (6)	C23—N5—C24—C25	-178.9 (4)
C7—C2—C3—C4	0.0 (6)	C23—C18—C19—C20	0.4 (7)
C7—C6—C5—C4	-0.4 (7)	C23—C22—C21—C20	0.0 (8)
C29—C17—C18—C23	-0.1 (6)	C24—N5—C23—C18	-0.9 (7)
C29—C17—C18—C19	-179.4 (4)	C24—N5—C23—C22	179.6 (4)
C29—C24—C25—C26	-0.3 (7)	C24—C29—C17—N4	179.5 (4)
C29—C28—C27—C26	-0.9 (8)	C24—C29—C17—C18	-0.6 (6)
C1—C2—C7—N2	-1.9 (6)	C24—C29—C28—C27	1.0 (7)
C1—C2—C7—C6	178.6 (4)	C24—C25—C26—C27	0.4 (8)
C1—C2—C3—C4	-179.3 (4)	C19—C18—C23—N5	-179.8 (4)
C1—C13—C8—N2	2.4 (6)	C19—C18—C23—C22	-0.3 (7)
C1—C13—C8—C9	-177.5 (4)	C28—C29—C17—N4	-0.6 (7)
C1—C13—C12—C11	178.2 (4)	C28—C29—C17—C18	179.4 (4)
C13—C8—C9—C10	-0.8 (7)	C28—C29—C24—N5	-179.4 (4)
C13—C12—C11—C10	-0.8 (7)	C28—C29—C24—C25	-0.3 (6)
C17—C29—C24—N5	0.6 (6)	C22—C21—C20—C19	0.1 (8)
C17—C29—C24—C25	179.6 (4)	C25—C26—C27—C28	0.2 (8)
C17—C29—C28—C27	-179.0 (5)	C16—N3—C14—O1	-177.2 (6)
C17—C18—C23—N5	0.9 (6)	C32—N6—C30—O2	177.7 (6)
C17—C18—C23—C22	-179.7 (4)	C15—N3—C14—O1	-0.8 (9)
C17—C18—C19—C20	179.7 (4)	C31—N6—C30—O2	-0.1 (10)

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>
N2—H2...O1	0.86	1.86	2.723 (5)	176
N4—H4 <i>A</i> ...C12	0.86	2.40	3.225 (3)	160
N4—H4 <i>B</i> ...C11	0.86	2.38	3.211 (4)	163
N1—H1 <i>A</i> ...C11	0.86	2.39	3.209 (3)	160
N1—H1 <i>B</i> ...C12	0.86	2.42	3.246 (3)	162
N5—H5 <i>A</i> ...O2	0.86	1.88	2.740 (5)	175