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Redetermination of adeninium dichloride: the question of centrosymmetry

Thomas C. Lewis and Derek A. Tocher*

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England

Correspondence e-mail: d.a.tocher@ucl.ac.uk

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The low-temperature redetermination of adeninium(2+) dichloride, $C_5H_7N_5^{2+}\cdot 2Cl^-$, obtained as part of an experimental polymorph screen on adenine, is reported here. The crystal structure is shown to be centrosymmetric. Cations and anions are connected through N—H···N and N—H···Cl hydrogen bonds [N···N = 2.899 (2) Å and N···Cl = 3.0274 (14)–3.5155 (16) Å] to form sheets perpendicular to the *b* axis.

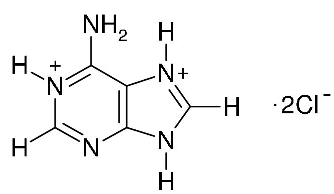
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.024
wR factor = 0.063
Data-to-parameter ratio = 11.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), is a hydrochloride salt of adenine, which is one of the two common purine bases found in ribose and deoxyribose nucleic acids.



(I)

The unit cell was determined in 1974 (Iwasaki, 1974); however, it was not possible unequivocally to establish the correct space group, either $Pna2_1$ or $Pnam$ (non-standard setting of $Pnma$), as refinement in each gave similar R values (0.043 and 0.045, respectively). The structure was also determined at room temperature by Kistenmacher & Shigematsu (1974), and refined in the centrosymmetric space group $Pnma$, giving an R value of 0.035. In this space group, mirror symmetry is imposed on the adenine dication, with some atoms having large r.m.s. displacements normal to the mirror plane. However, it was argued that purines commonly show some bending about the C2—C3 bond axis (Sletten & Jessen, 1969), which is inconsistent with the analysis in the centrosymmetric space group. Hence, it was suggested that the true space group could be $Pn2_1a$ (non-standard setting of $Pna2_1$).We have redetermined the crystal structure at 150 K, to gain more precise data for our molecular modelling studies. The structure was refined in both $Pnma$ and $Pna2_1$, giving R values of 0.0241 and 0.0229, respectively, despite the statistical averages for the normalized structure factors (E values) being more consistent with a centrosymmetric than a non-centrosymmetric distribution. However, when refined in the non-centrosymmetric space group, all the ring H atoms deviate by between 13–15° from the mean ring plane to which they are attached. These are large deviations when compared with other adeninium crystal structures, which include adeninium

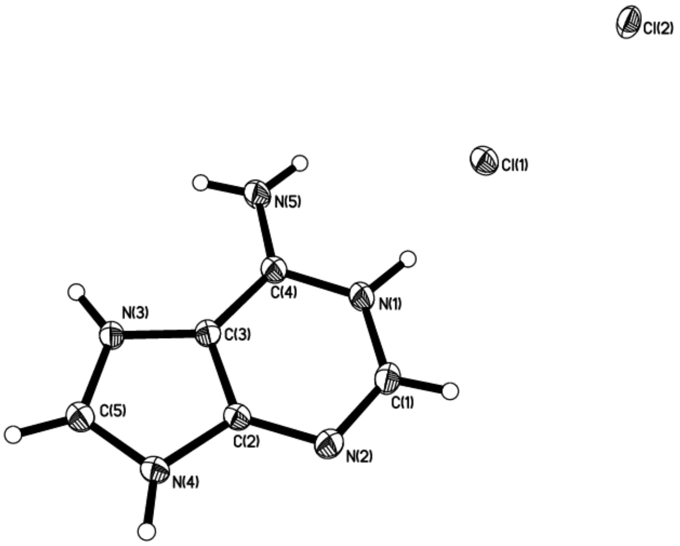


Figure 1
View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

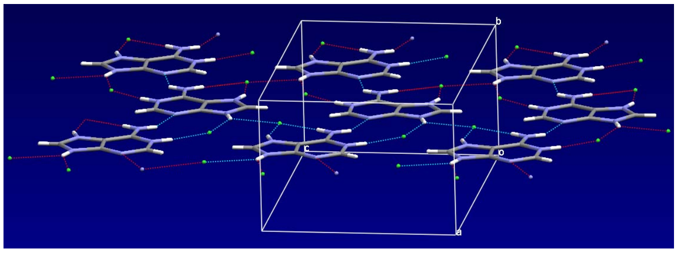


Figure 2
View of the hydrogen-bonded sheet motif present in (I), with the hydrogen bonds shown as dotted lines; $D\cdots A$ distances greater than 3.3 Å have been omitted for clarity.

sulfate (Langer & Huml, 1978), adeninium dinitrate (Hardgrove *et al.*, 1983) and adeninium diperchlorate monohydrate (Bendjeddou *et al.*, 2003). In addition, analysing the non-centrosymmetric structure with *PLATON* (Spek, 2003) to search for missing or higher symmetry gave the centrosymmetric structure at 100% confidence level. Hence, using the superior low-temperature data, we can conclude that the most likely space group of (I) is *Pnma*.

In this low-temperature determination, the precision of the unit-cell dimensions was improved by an order of magnitude, and the unit-cell volume decreased by *ca* 14 Å^3, consistent with the determination at low temperature. In general, the metric parameters are not significantly different, within standard deviations, from those found at room temperature. The adenine molecule is protonated at N1 and N3, with the C—N bond lengths in the rings in the range 1.308 (2)–1.375 (2) Å, and the C2—C3, C3—C4 and C4—N5 bond lengths being 1.379 (2), 1.409 (2) and 1.310 (2) Å, respectively. In the crystal structure, the cations are linked through N—H$\cdots$N hydrogen bonds to form extended chains in the *a*-axis direction. These chains are, in turn, linked by N—H$\cdots$Cl hydrogen bonds to form sheets (Fig. 2) lying parallel to the (040) family of lattice planes. Four of the H atoms on the adenine cation are involved in N—H$\cdots$Cl hydrogen bonds (see Table 1) and, in addition, atoms H4 and H6 are involved in weaker bifurcated N—H$\cdots$Cl hydrogen bonds, with N$\cdots$Cl distances of 3.2936 (15) and 3.5155 (16) Å, respectively. There are two independent Cl^- ions within the hydrogen-bonded sheets: Cl1, which is involved in one conventional and three weaker bifurcated N—H$\cdots$Cl hydrogen bonds, and Cl2, which is involved in three conventional N—H$\cdots$Cl hydrogen bonds. In the N—H$\cdots$N and N—H$\cdots$Cl hydrogen-bonded sheets, all acceptors and donors are used.

Experimental

As part of an experimental polymorph screen on adenine, (I) was obtained by evaporation of a solution of equimolecular amounts of thymine/adenine, and cytosine/adenine in dilute hydrochloric acid, giving colourless block-shaped crystals.

Crystal data

$C_5H_7N_5^{2+}\cdot 2Cl^-$
M_r = 208.06
Orthorhombic, *Pnma*
a = 13.4405 (11) Å
b = 6.4774 (5) Å
c = 9.3684 (7) Å
V = 815.61 (11) Å^3
Z = 4
D_x = 1.694 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5209 reflections
θ = 2.7–28.1°
μ = 0.74 mm^{-1}
T = 150 (2) K
Block, colourless
0.74 × 0.26 × 0.24 mm

Data collection

Bruker SMART APEX diffractometer
Narrow-frame ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.609, T_{max} = 0.842
6736 measured reflections
1076 independent reflections
1064 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 28.3°
$h = -17 \rightarrow 17$
$k = -8 \rightarrow 8$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.063
S = 0.99
1076 reflections
94 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.5379P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H2$\cdots$Cl1	0.94 (3)	2.11 (3)	3.0274 (14)	167 (2)
N3—H3$\cdots$Cl2^{i}	0.89 (3)	2.25 (3)	3.0693 (14)	153 (2)
N4—H4$\cdots$Cl1^{ii}	0.90 (2)	2.53 (2)	3.2936 (15)	143.8 (19)
N4—H4$\cdots$Cl2^{ii}	0.90 (2)	2.56 (2)	3.1695 (14)	126.1 (18)
N5—H6$\cdots$N2^{iii}	0.85 (2)	2.28 (2)	2.899 (2)	129.6 (19)
N5—H6$\cdots$Cl1	0.85 (2)	2.82 (2)	3.5155 (16)	140.3 (18)
N5—H7$\cdots$Cl2^{i}	0.88 (3)	2.22 (3)	3.0985 (16)	175 (2)

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

H atoms were refined independently using an isotropic model.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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Adeninium(2+) dichloride

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$C_5H_7N_5^{2+}\cdot 2Cl^-$
$M_r = 208.06$
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
$a = 13.4405$ (11) Å
$b = 6.4774$ (5) Å
$c = 9.3684$ (7) Å
$V = 815.61$ (11) Å^3
$Z = 4$
$F(000) = 424$
$D_x = 1.694$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5209 reflections
$\theta = 2.7$–28.1°
$\mu = 0.74$ mm^{-1}
$T = 150$ K
Block, colourless
0.74 × 0.26 × 0.24 mm

Data collection

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Radiation source: fine-focus sealed tube
Graphite monochromator
ω rotation scans with narrow frames
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$T_{min} = 0.609$, $T_{max} = 0.842$
6736 measured reflections
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1064 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.7°$
$h = -17\rightarrow17$
$k = -8\rightarrow8$
$l = -12\rightarrow12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.063$
$S = 0.99$
1076 reflections
94 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.5379P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

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

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

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.19853 (3)	0.2500	0.44260 (4)	0.02093 (12)
Cl2	0.06411 (3)	0.2500	0.11040 (4)	0.02752 (14)
N1	0.32438 (10)	0.2500	0.71060 (15)	0.0199 (3)
N2	0.47861 (10)	0.2500	0.83213 (15)	0.0216 (3)
N3	0.29232 (10)	0.2500	1.09822 (14)	0.0180 (3)
N4	0.45453 (10)	0.2500	1.09002 (15)	0.0187 (3)
N5	0.16825 (10)	0.2500	0.81532 (16)	0.0233 (3)
C1	0.42539 (12)	0.2500	0.71522 (18)	0.0225 (3)
C2	0.42189 (11)	0.2500	0.95093 (16)	0.0163 (3)
C3	0.31936 (11)	0.2500	0.95674 (17)	0.0164 (3)
C4	0.26529 (12)	0.2500	0.82791 (16)	0.0172 (3)
C5	0.37495 (12)	0.2500	1.17584 (17)	0.0199 (3)
H1	0.4584 (17)	0.2500	0.631 (2)	0.026 (5)*
H2	0.2946 (18)	0.2500	0.620 (3)	0.034 (6)*
H3	0.231 (2)	0.2500	1.133 (3)	0.042 (7)*
H4	0.5164 (18)	0.2500	1.125 (2)	0.026 (6)*
H5	0.3745 (14)	0.2500	1.277 (2)	0.018 (5)*
H6	0.1424 (16)	0.2500	0.733 (3)	0.022 (5)*
H7	0.1355 (17)	0.2500	0.896 (3)	0.033 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0201 (2)	0.0261 (2)	0.0166 (2)	0.000	−0.00298 (13)	0.000
Cl2	0.0153 (2)	0.0514 (3)	0.0159 (2)	0.000	0.00137 (13)	0.000
N1	0.0170 (6)	0.0298 (7)	0.0129 (6)	0.000	−0.0016 (5)	0.000
N2	0.0144 (6)	0.0323 (8)	0.0179 (7)	0.000	0.0012 (5)	0.000
N3	0.0145 (6)	0.0264 (7)	0.0130 (6)	0.000	0.0004 (5)	0.000
N4	0.0140 (6)	0.0261 (7)	0.0159 (6)	0.000	−0.0024 (5)	0.000
N5	0.0145 (6)	0.0406 (9)	0.0150 (7)	0.000	−0.0034 (5)	0.000
C1	0.0175 (8)	0.0351 (9)	0.0150 (7)	0.000	0.0024 (6)	0.000
C2	0.0148 (7)	0.0197 (7)	0.0145 (7)	0.000	−0.0015 (5)	0.000
C3	0.0148 (7)	0.0202 (7)	0.0142 (7)	0.000	0.0000 (5)	0.000
C4	0.0160 (7)	0.0211 (7)	0.0146 (7)	0.000	−0.0009 (5)	0.000
C5	0.0174 (7)	0.0261 (8)	0.0161 (7)	0.000	−0.0007 (6)	0.000

Geometric parameters (Å, º)

N1—C4	1.356 (2)	N4—C2	1.375 (2)
N1—C1	1.358 (2)	N4—H4	0.90 (2)

N1—H2	0.94 (3)	N5—C4	1.310 (2)
N2—C1	1.308 (2)	N5—H6	0.85 (2)
N2—C2	1.349 (2)	N5—H7	0.88 (3)
N3—C5	1.327 (2)	C1—H1	0.91 (2)
N3—C3	1.374 (2)	C2—C3	1.379 (2)
N3—H3	0.89 (3)	C3—C4	1.409 (2)
N4—C5	1.338 (2)	C5—H5	0.95 (2)
C4—N1—C1	124.03 (15)	N2—C1—H1	117.5 (14)
C4—N1—H2	118.9 (15)	N1—C1—H1	117.5 (14)
C1—N1—H2	117.1 (15)	N2—C2—N4	126.98 (14)
C1—N2—C2	112.44 (13)	N2—C2—C3	126.67 (14)
C5—N3—C3	107.88 (14)	N4—C2—C3	106.35 (14)
C5—N3—H3	125.3 (17)	N3—C3—C2	107.60 (14)
C3—N3—H3	126.9 (17)	N3—C3—C4	133.61 (15)
C5—N4—C2	108.32 (13)	C2—C3—C4	118.80 (14)
C5—N4—H4	121.5 (14)	N5—C4—N1	120.68 (15)
C2—N4—H4	130.2 (14)	N5—C4—C3	126.22 (15)
C4—N5—H6	119.3 (14)	N1—C4—C3	113.09 (13)
C4—N5—H7	114.9 (15)	N3—C5—N4	109.86 (14)
H6—N5—H7	126 (2)	N3—C5—H5	122.9 (11)
N2—C1—N1	124.98 (16)	N4—C5—H5	127.3 (11)
C2—N2—C1—N1	0.0	N2—C2—C3—C4	0.0
C4—N1—C1—N2	0.0	N4—C2—C3—C4	180.0
C1—N2—C2—N4	180.0	C1—N1—C4—N5	180.0
C1—N2—C2—C3	0.0	C1—N1—C4—C3	0.0
C5—N4—C2—N2	180.0	N3—C3—C4—N5	0.0
C5—N4—C2—C3	0.0	C2—C3—C4—N5	180.0
C5—N3—C3—C2	0.0	N3—C3—C4—N1	180.0
C5—N3—C3—C4	180.0	C2—C3—C4—N1	0.0
N2—C2—C3—N3	180.0	C3—N3—C5—N4	0.0
N4—C2—C3—N3	0.0	C2—N4—C5—N3	0.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···Cl1	0.94 (3)	2.11 (3)	3.0274 (14)	167 (2)
N3—H3···Cl2^{i}	0.89 (3)	2.25 (3)	3.0693 (14)	153 (2)
N4—H4···Cl1^{ii}	0.90 (2)	2.53 (2)	3.2936 (15)	144 (2)
N4—H4···Cl2^{ii}	0.90 (2)	2.56 (2)	3.1695 (14)	126 (2)
N5—H6···N2^{iii}	0.85 (2)	2.28 (2)	2.899 (2)	130 (2)
N5—H6···Cl1	0.85 (2)	2.82 (2)	3.5155 (16)	140 (2)
N5—H7···Cl2^{i}	0.88 (3)	2.22 (3)	3.0985 (16)	175 (2)

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*+1/2, *y*, −*z*+3/2; (iii) *x*−1/2, *y*, −*z*+3/2.