Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Putrescinium dichloride: a redetermination at 100 K

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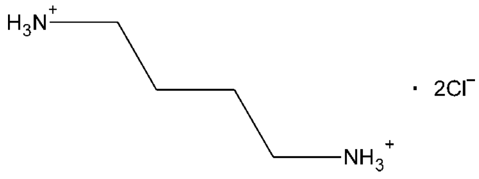
Received 18 June 2007; accepted 28 June 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.037; wR factor = 0.085; data-to-parameter ratio = 14.9.

The crystal structure of the title compound, $C_4H_{14}N_2^{2+}\cdot 2Cl^-$, has been redetermined at 100 (1) K. In the room-temperature structure [Chandrasekhar & Pattabhi (1980). *Acta Cryst.* B**36**, 2486–2488], the H atoms were located but their parameters were not refined. Since the hydrogen bonds in this structure are extensive, the H-atom positions are of primary importance. The dication lies on a centre of symmetry and the N atoms are slightly displaced [0.019 (4) Å] from the plane of the four C atoms. N—H⋯Cl and C—H⋯Cl hydrogen bonds form a three-dimensional network.

Related literature

For related literature, see: Ashida & Hirokawa (1963); Karigiannis & Papaioannou (2000); Radecka-Paryzek *et al.* (2007).



Experimental

Crystal data

$C_4H_{14}N_2^{2+}\cdot 2Cl^-$
M_r = 161.07
Monoclinic, $P2_1/c$
a = 4.5625 (9) Å
b = 8.3514 (16) Å
c = 10.696 (2) Å
β = 92.472 (16)°
V = 407.16 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.71 mm^{-1}
T = 100 (1) K
0.3 × 0.15 × 0.1 mm

Data collection

Kuma KM4 CCD four-circle diffractometer
Absorption correction: none
2576 measured reflections
970 independent reflections
716 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.085
S = 1.06
970 reflections
65 parameters
All H-atom parameters refined
$\Delta\rho_{\rm max}$ = 0.52 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.43 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1C⋯Cl1	0.85 (3)	2.53 (3)	3.269 (2)	145 (2)
C3—H3B⋯Cl1	1.02 (2)	2.83 (2)	3.624 (2)	135.0 (17)
N1—H1A⋯Cl1$^{\rm i}$	0.86 (2)	2.38 (3)	3.192 (2)	156 (2)
N1—H1B⋯Cl1$^{\rm ii}$	0.90 (3)	2.39 (3)	3.250 (2)	159 (2)
C3—H3A⋯Cl1$^{\rm ii}$	1.03 (2)	2.80 (2)	3.659 (2)	140.2 (17)
N1—H1C⋯Cl1$^{\rm iii}$	0.85 (3)	2.82 (3)	3.258 (2)	114 (2)
C2—H2A⋯Cl1$^{\rm iv}$	1.01 (2)	2.81 (2)	3.816 (2)	177.0 (17)
C2—H2B⋯Cl1$^{\rm v}$	0.97 (2)	3.00 (2)	3.952 (2)	166.3 (17)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2183).

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Ashida, T. & Hirokawa, S. (1963). *Bull. Chem. Soc. Jpn*, **36**, 704–707.
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doi:10.1107/S160053680703156X

supplementary materials

Acta Cryst. (2007). E**63**, o3650 [**doi:10.1107/S160053680703156X**]

Putrescinium dichloride: a redetermination at 100 K

I. Pospieszna-Markiewicz, **W. Radecka-Paryzek** and **M. Kubicki**

Comment

Putrescine is involved in proliferation and differentiation of cells in DNA replication and membrane stabilization, in addition to being present in high intercellular concentration in carcinogenetic states of cells. The negative charge of the DNA backbone makes it target for cationic species, so positively charged putrescine and the other biogenic polyamines may interact directly with DNA (Karigiannis & Papaioannou, 2000). During our study on design and synthesis of self-assembled supramolecular architectures incorporating biogenic polyamine fragments with flexibility and strong affinity to nucleic acids, therefore displaying interesting properties and potential applications (Radecka-Paryzek *et al.*, 2007), we isolated the crystals of putrescine dichloride.

The crystal structure of putrescinium chloride was investigated by Ashida & Hirokawa (1963) using visually estimated intensities, and then by Chandrasekhar & Pattabhi (1980). This last determination was performed at room temperature, and H atom positions and thermal parameters were not refined. *R* factor of this determination was also quite high, 6.4%. The hydrogen bond system is extensive in this crystal structure, so the positions of H atoms are important. We have repeated this structure determination at 100 (1) K and with the new data we were able to refine all parameters of H atoms. The overall features of the crystal structure are similar to those of Ashida & Hirokawa (1963). The elongation of the bond lengths at 100 K is probably connected with the minimalization of libration effect. The N—H···Cl and C—H···Cl hydrogen bonds connect cations and anions into layers (Fig. 2). These layers in turn by means of electrostatic interactions and weaker C—H···Cl hydrogen bonds make a three-dimensional structure with alternate cation and anion layers (Fig. 3).

Experimental

The title compound was isolated during the slow diffusion of dioxane into a methanol solution of the lanthanum(III) chloride Schiff base complex – product of the template condensation reaction of one molecule of putrescine with two molecules of salicylaldehyde.

Refinement

H atoms were located in a difference Fourier map and freely refined.

Figures

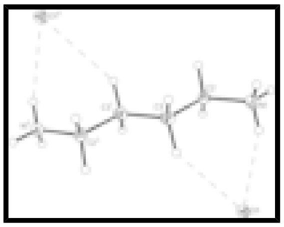

Fig. 1. Anisotropic displacement ellipsoid representation at the 50% probability level (Siemens, 1989) of the title compound, with atom-numbering scheme. The H atoms are drawn as spheres of arbitrary radius. Hydrogen bonds are depicted as dashed lines [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$].

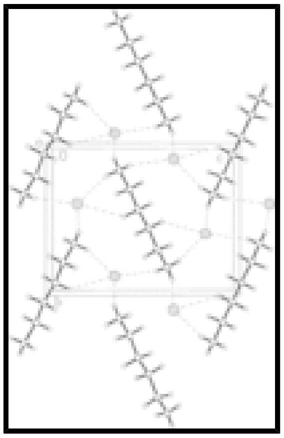

Fig. 2. Hydrogen-bonded layer as seen along the *a* axis. Hydrogen bonds are depicted as dashed lines.

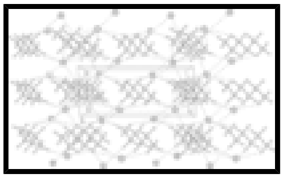

Fig. 3. Crystal packing viewed along the *b* axis. Hydrogen bonds and weaker C—H···Cl contacts are depicted as dashed lines.

Butane-1,4-diyldiammonium dichloride

Crystal data

$C_4H_{14}N_2^{2+}\cdot 2Cl^-$

$M_r = 161.07$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 4.5625 (9)$ Å

$b = 8.3514 (16)$ Å

$c = 10.696 (2)$ Å

$\beta = 92.472 (16)$°

$V = 407.16 (14)$ Å^3

$Z = 2$

$F_{000} = 172$

$D_x = 1.314$ Mg m^{-3}

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

Cell parameters from 1321 reflections

$\theta = 3–25$°

$\mu = 0.71$ mm^{-1}

$T = 100 (1)$ K

Prism, colourless

0.3 × 0.15 × 0.1 mm

Data collection

Kuma KM4 CCD four-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100(1)$ K

ω scans

Absorption correction: none

2576 measured reflections

970 independent reflections

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

$R_{\text{int}} = 0.045$

$\theta_{\text{max}} = 28.0$°

$\theta_{\text{min}} = 3.1$°

$h = -6\rightarrow 5$

$k = -9\rightarrow 11$

$l = -14\rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	All H-atom parameters refined
$wR(F^2) = 0.085$	$w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\max} < 0.001$
970 reflections	$\Delta\rho_{\max} = 0.52$ e Å^{-3}
65 parameters	$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 > 2sigma(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}
N1	0.6183 (4)	0.1691 (3)	0.37234 (18)	0.0161 (4)
H1A	0.516 (5)	0.089 (3)	0.345 (2)	0.013 (6)*
H1B	0.714 (6)	0.209 (3)	0.307 (2)	0.033 (7)*
H1C	0.751 (6)	0.141 (3)	0.426 (3)	0.029 (7)*
C2	0.4232 (5)	0.2942 (3)	0.4245 (2)	0.0149 (5)
H2A	0.275 (5)	0.325 (3)	0.356 (2)	0.013 (5)*
H2B	0.319 (5)	0.247 (3)	0.492 (2)	0.019 (6)*
C3	0.6007 (5)	0.4371 (3)	0.4727 (2)	0.0156 (5)
H3A	0.713 (5)	0.483 (3)	0.399 (2)	0.019 (6)*
H3B	0.754 (5)	0.397 (3)	0.538 (2)	0.020 (6)*
Cl1	0.87455 (11)	0.10103 (6)	0.65756 (5)	0.01548 (18)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0167 (10)	0.0156 (10)	0.0160 (9)	−0.0009 (8)	0.0007 (8)	−0.0012 (8)
C2	0.0149 (11)	0.0153 (11)	0.0147 (10)	0.0021 (9)	0.0014 (8)	−0.0008 (9)
C3	0.0142 (11)	0.0184 (13)	0.0141 (11)	−0.0006 (9)	0.0011 (8)	−0.0007 (9)

Cl1	0.0164 (3)	0.0166 (3)	0.0135 (3)	0.0006 (2)	0.00115 (17)	−0.0010 (2)

Geometric parameters (Å, °)

N1—C2	1.496 (3)	C2—H2A	1.01 (2)
N1—H1A	0.86 (2)	C2—H2B	0.97 (2)
N1—H1B	0.90 (3)	C3—C3^{i}	1.528 (4)
N1—H1C	0.85 (3)	C3—H3A	1.03 (2)
C2—C3	1.520 (3)	C3—H3B	1.02 (2)
C2—N1—H1A	110.6 (16)	N1—C2—H2B	108.2 (15)
C2—N1—H1B	110.3 (17)	C3—C2—H2B	109.9 (14)
H1A—N1—H1B	107 (2)	H2A—C2—H2B	108.1 (18)
C2—N1—H1C	110.8 (19)	C2—C3—C3^{i}	110.4 (2)
H1A—N1—H1C	112 (2)	C2—C3—H3A	108.0 (13)
H1B—N1—H1C	106 (2)	C3^{i}—C3—H3A	111.3 (14)
N1—C2—C3	110.96 (17)	C2—C3—H3B	108.4 (14)
N1—C2—H2A	107.4 (13)	C3^{i}—C3—H3B	111.7 (14)
C3—C2—H2A	112.2 (13)	H3A—C3—H3B	107.0 (18)
N1—C2—C3—C3^{i}	−179.2 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···Cl1	0.85 (3)	2.53 (3)	3.269 (2)	145 (2)
C3—H3B···Cl1	1.02 (2)	2.83 (2)	3.624 (2)	135.0 (17)
N1—H1A···Cl1^{ii}	0.86 (2)	2.38 (3)	3.192 (2)	156 (2)
N1—H1B···Cl1^{iii}	0.90 (3)	2.39 (3)	3.250 (2)	159 (2)
C3—H3A···Cl1^{iii}	1.03 (2)	2.80 (2)	3.659 (2)	140.2 (17)
N1—H1C···Cl1^{iv}	0.85 (3)	2.82 (3)	3.258 (2)	114 (2)
C2—H2A···Cl1^{v}	1.01 (2)	2.81 (2)	3.816 (2)	177.0 (17)
C2—H2B···Cl1^{vi}	0.97 (2)	3.00 (2)	3.952 (2)	166.3 (17)

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

Fig. 1

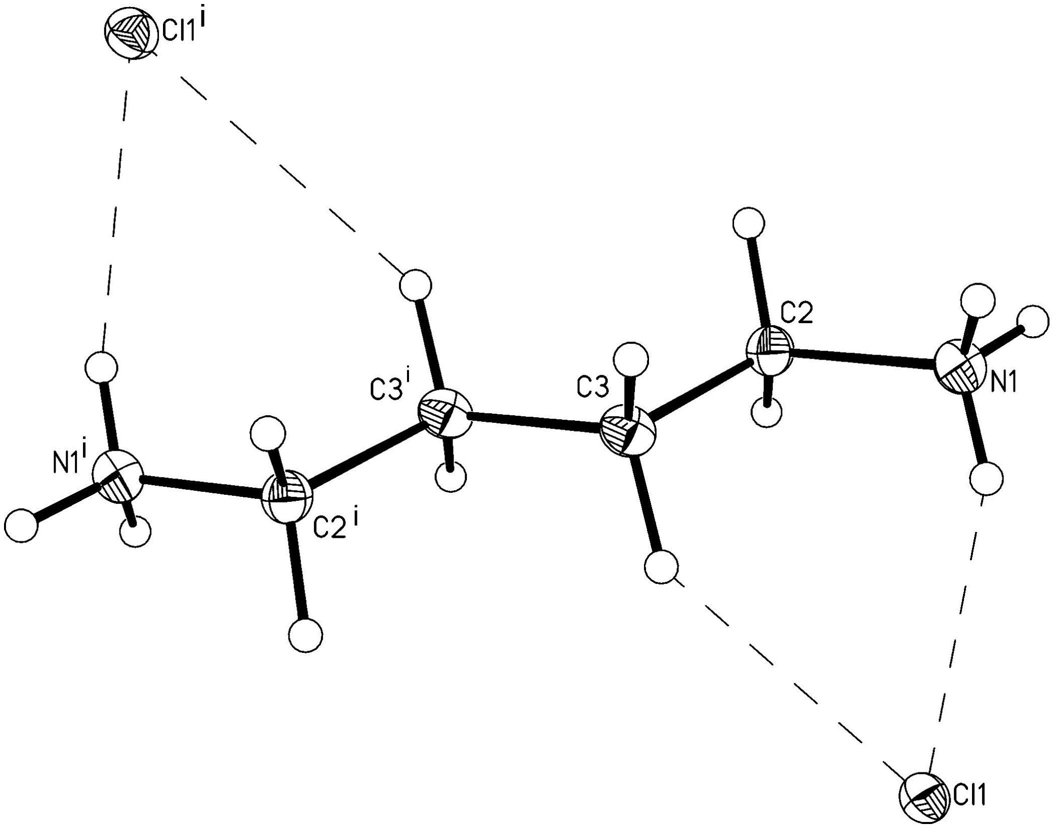

Fig. 2

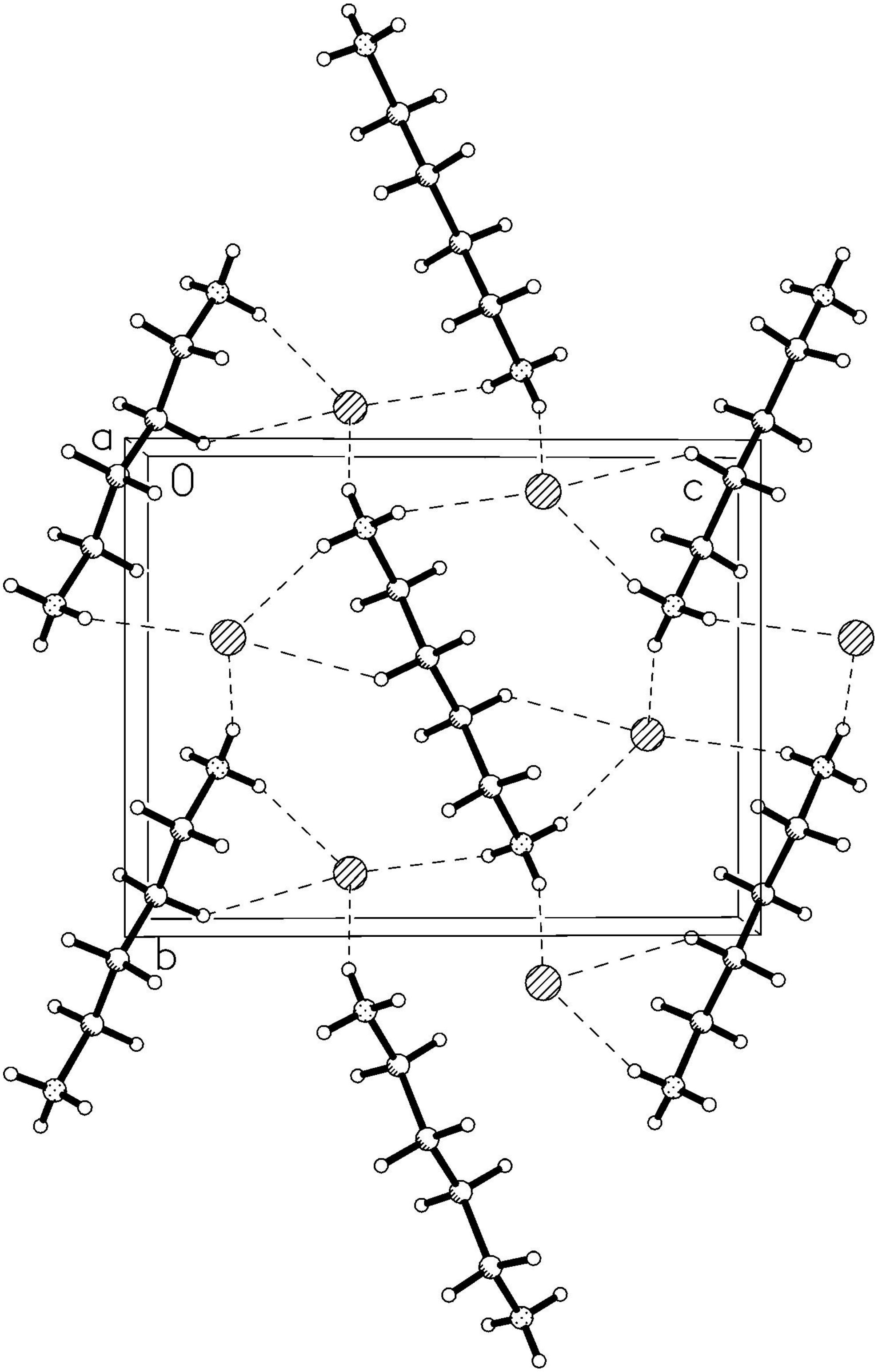

Fig. 3