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Crystal structure of *N*,*N*′-bis(pyridin-3-ylmethyl)-cyclohexane-1,4-diammonium dichloride

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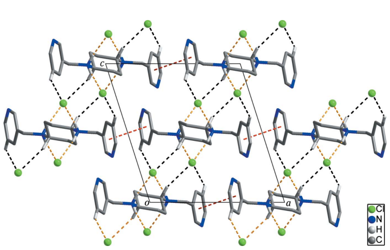
The title salt, $C_{18}H_{26}N_4^{2+}\cdot 2Cl^-$, was obtained by the protonation of *N*,*N*-bis(pyridin-4-ylmethyl)cyclohexane-1,4-diamine with hydrochloric acid in ethanol. The asymmetric unit consists of one half of an *N*,*N*-bis(pyridin-3-ylmethyl)cyclohexane-1,4-diammonium dication, with a crystallographic inversion centre located at the centre of the cyclohexyl ring, and a chloride anion. The central cyclohexyl ring in the dication adopts a chair conformation. The two *trans*-(4-pyridine)–CH_2–NH_2– moieties at the 1- and 4-positions of the central cyclohexyl ring occupy equatorial sites. The terminal pyridine ring is tilted by 53.72 (6)° with respect to the mean plane of the central cyclohexyl ring (r.m.s. deviation = 0.2413 Å). In the crystal, $N^+—H\cdots Cl^-$ hydrogen bonds between the dications and the chloride anions, and π–π stacking interactions between the pyridine rings of the dications afford a two-dimensional sheet extending parallel to the *ab* plane. These sheets are further connected through weak $C—H\cdots Cl^-$ hydrogen bonds, resulting in the formation of a three-dimensional supramolecular network.

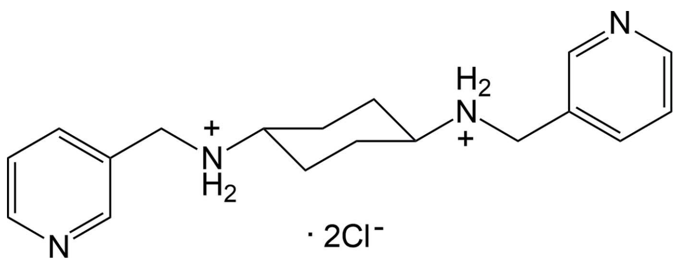


1. Chemical context

Several dipyridyl-type ligands with or without a central section between the terminal pyridine rings have contributed greatly to the development of metal–organic coordination polymers with intriguing topologies or potential applications (Silva *et al.*, 2015; Furukawa *et al.*, 2014; Robin & Fromm, 2006; Robson, 2008; Leong & Vittal, 2011). Our group has also tried to prepare extended dipyridyl-type ligands with a bulky central moiety for the construction of versatile coordination polymers. Recently, we prepared the dipyridyl-type ligand containing 4-pyridine terminal groups and a cyclohexyl ring as a bulky central moiety, namely *N*,*N*-bis(pyridin-4-ylmethyl)cyclohexane-1,4-diamine, and reported the crystal structure of its chloride salt (Moon *et al.*, 2016). As an extension of our research, we have prepared a dipyridyl-type ligand with central cyclohexyl ring and 3-pyridine terminal groups, namely *N*,*N*-bis(pyridin-3-ylmethyl)cyclohexane-1,4-diamine, synthesized by a condensation reaction between 1,4-cyclohexanediamine and 3-pyridinecarboxaldehyde according to the literature procedure (Huh & Lee, 2007). Herein we report on crystal structure of the title salt obtained by the protonation of both amine groups in this molecule.

2. Structural commentary

Fig. 1 shows the molecular structure of the title salt, which lies about an inversion centre located at the centre of the cyclohexyl ring. Therefore, the asymmetric unit comprises one half of the N,N-bis(pyridin-3-ylmethyl)cyclohexane-1,4-diammonium dication and a chloride anion. In the dication, the central cyclohexyl ring displays a chair conformation and the two *trans*-(4-pyridine)–CH_2–NH_2– moieties occupy equatorial sites at the 1- and 4-positions of the central cyclohexyl ring. The terminal pyridine ring is tilted by 53.72 (6)° with respect to the mean plane of the cyclohexyl ring (r.m.s. deviation = 0.2413 Å). This tilting angle is larger than that [27.98 (5)°] of the similar dication with 4-pyridine rings as the terminal groups (Moon *et al.*, 2016).



3. Supramolecular features

In the crystal, N^+–H···Cl^- hydrogen bonds, Table 1 (yellow dashed lines in Figs. 2 and 3), between the dications and the chloride anions lead to the formation of chains along the *b* axis. Adjacent chains are additionally connected through intermolecular π–π stacking interactions [centroid-to-centroid distance = 3.8197 (8) Å] between the pyridine rings (red dashed lines in Figs. 2 and 3), resulting in the formation of a sheet extending parallel to the *ab* plane. These sheets are linked by weak C–H···Cl^- hydrogen bonds, Table 1 (black dashed lines in Fig. 3), between the dications and the chloride anions, forming a three-dimensional supramolecular network.

4. Database survey

A search of the Cambridge Structural Database (Version 5.37, Feb 2016 with two updates; Groom *et al.*, 2016) revealed only a Co^{II} complex with the dication of the title salt as a ligand, namely *catena*-[bis(μ^2-N,N'-bis(pyridin-3-ylmethyl)cyclohexane-1,4-diaminium)(nitrato-O,O')cobalt(II) pentanitrate methanol solvate] (Lee & Lee, 2010). Each Co^{II} ion in this

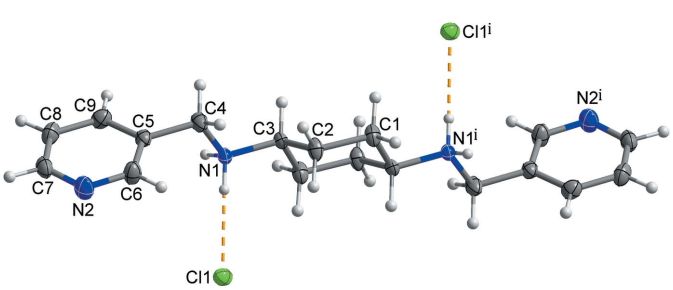


Figure 1
A view of the molecular structure of the title salt, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius and yellow dashed lines represent the intermolecular N^+—H···Cl^- hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1	0.891 (15)	2.237 (15)	3.1215 (10)	171.7 (12)
N1—H1B···Cl1^{i}	0.876 (16)	2.287 (16)	3.1588 (10)	173.8 (13)
C3—H3···Cl1^{ii}	1.00	2.76	3.7106 (11)	158
C8—H8···Cl1^{iii}	0.95	2.76	3.6020 (13)	148

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

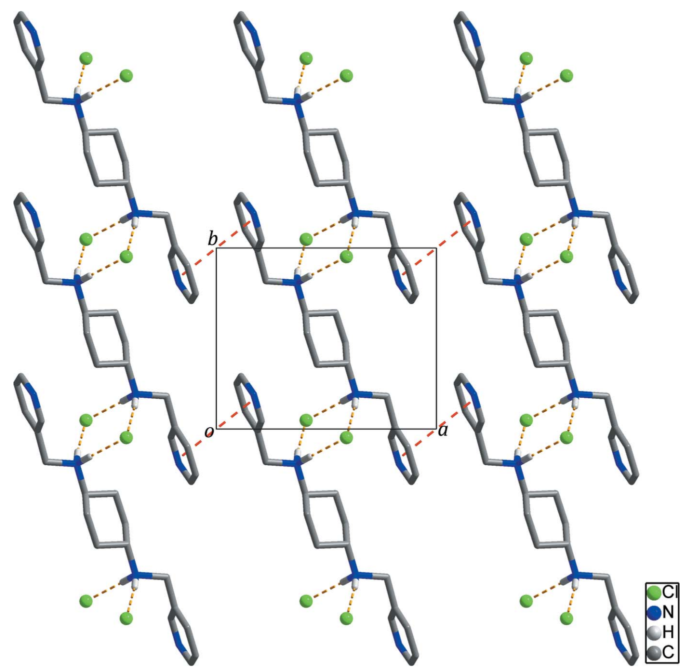


Figure 2
The two-dimensional sheet of the title salt formed through intermolecular N^+—H···Cl^- hydrogen bonds (yellow dashed lines) between the dications and the chloride anions and π–π stacking interactions (red dashed lines) between the pyridine rings of dications. H atoms not involved in intermolecular interactions have been omitted for clarity.

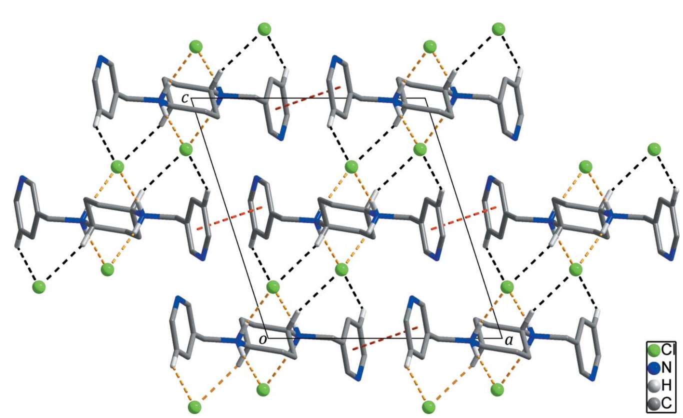


Figure 3
The three-dimensional supramolecular network of the title salt formed through intermolecular C—H···Cl^- hydrogen bonds (black dashed lines) between the two-dimensional sheets constructed by intermolecular N^+—H···Cl^- hydrogen bonds (yellow dashed lines) and π–π stacking interactions (red dashed lines). H atoms not involved in intermolecular interactions have been omitted for clarity.

complex is six-coordinated by two O atoms of one nitrate anion and four N atoms of four dipyridyl-type dication ligands to form a distorted octahedral geometry.

5. Synthesis and crystallization

N,*N*-bis(pyridin-3-ylmethylene)cyclohexane-1,4-diamine, prepared according to a literature method (Huh & Lee, 2007), was dissolved in ethanol, and then the pH was adjusted to 4–5 with 2 *M* hydrochloric acid. The resultant mixture was left to evaporate slowly over several days, resulting in the formation of X-ray quality single crystals of the title salt.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The position of the pyridine nitrogen atom was determined by the difference in the displacement parameters. All C-bound H atoms were positioned geometrically [with d(C—H) = 0.95 Å for Csp^2—H, 0.99 Å for methylene, 1.00 Å for methine H atoms] and were refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H atoms involved in hydrogen bonds were located in difference Fourier maps and refined freely [N—H = 0.891 (15) and 0.876 (16) Å].

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{26}N_4^{2+}\cdot 2Cl^-$
M_r	369.33
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	173
a, b, c (Å)	10.4637 (2), 8.1942 (2), 11.2797 (2)
β (°)	107.812 (1)
V (Å^3)	920.78 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.36
Crystal size (mm)	0.32 × 0.27 × 0.21
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker 2013)
T_{min}, T_{max}	0.671, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8881, 2303, 2118
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.083, 1.03
No. of reflections	2303
No. of parameters	117
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 2010).

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supporting information

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Crystal structure of *N*,*N*′-bis(pyridin-3-ylmethyl)cyclohexane-1,4-diammonium dichloride

Suk-Hee Moon, Hansu Im, Tae Ho Kim and Ki-Min Park

Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

N,*N*′-Bis(pyridin-3-ylmethyl)cyclohexane-1,4-diammonium dichloride

Crystal data

$C_{18}H_{26}N_4^{2+}\cdot 2Cl^-$
$M_r = 369.33$
Monoclinic, $P2_1/n$
$a = 10.4637$ (2) Å
$b = 8.1942$ (2) Å
$c = 11.2797$ (2) Å
$\beta = 107.812$ (1)°
$V = 920.78$ (3) Å^3
$Z = 2$
$F(000) = 392$
$D_x = 1.332$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4678 reflections
$\theta = 2.3$–28.4°
$\mu = 0.36$ mm^{-1}
$T = 173$ K
Block, colourless
0.32 × 0.27 × 0.21 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker 2013)
$T_{min} = 0.671$, $T_{max} = 0.746$
8881 measured reflections
2303 independent reflections
2118 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.4°$, $\theta_{min} = 2.3°$
$h = -12 \rightarrow 14$
$k = -9 \rightarrow 10$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.083$
$S = 1.03$
2303 reflections
117 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.3189P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.40846 (3)	0.04783 (3)	0.28633 (2)	0.02513 (10)
N1	0.63461 (9)	0.19285 (11)	0.51048 (9)	0.01829 (19)
H1A	0.5756 (14)	0.1538 (18)	0.4416 (13)	0.021 (3)*
H1B	0.6295 (14)	0.1263 (19)	0.5696 (14)	0.026 (4)*
N2	0.83020 (13)	−0.19199 (14)	0.33231 (10)	0.0343 (3)
C1	0.54173 (12)	0.64376 (14)	0.44414 (11)	0.0240 (2)
H1C	0.6086	0.6937	0.5170	0.029*
H1D	0.5352	0.7127	0.3704	0.029*
C2	0.58760 (13)	0.47226 (14)	0.42261 (11)	0.0236 (2)
H2A	0.5242	0.4254	0.3462	0.028*
H2B	0.6773	0.4780	0.4106	0.028*
C3	0.59394 (11)	0.36313 (13)	0.53315 (10)	0.0180 (2)
H3	0.6618	0.4083	0.6089	0.022*
C4	0.77439 (12)	0.18178 (15)	0.50226 (12)	0.0265 (3)
H4A	0.8381	0.2237	0.5804	0.032*
H4B	0.7819	0.2515	0.4330	0.032*
C5	0.81211 (11)	0.00954 (14)	0.48115 (10)	0.0207 (2)
C6	0.79449 (14)	−0.04487 (16)	0.36097 (12)	0.0298 (3)
H6	0.7541	0.0278	0.2944	0.036*
C7	0.88687 (13)	−0.29136 (15)	0.42730 (12)	0.0289 (3)
H7	0.9154	−0.3959	0.4092	0.035*
C8	0.90643 (13)	−0.25138 (16)	0.54997 (12)	0.0299 (3)
H8	0.9454	−0.3275	0.6144	0.036*
C9	0.86810 (13)	−0.09778 (16)	0.57749 (11)	0.0271 (3)
H9	0.8801	−0.0667	0.6613	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02754 (17)	0.02485 (16)	0.02046 (15)	−0.00212 (10)	0.00355 (11)	0.00078 (9)
N1	0.0189 (5)	0.0152 (4)	0.0209 (4)	0.0013 (3)	0.0064 (4)	−0.0008 (3)
N2	0.0445 (7)	0.0312 (6)	0.0274 (5)	0.0077 (5)	0.0114 (5)	−0.0051 (4)
C1	0.0265 (6)	0.0173 (5)	0.0333 (6)	0.0025 (4)	0.0168 (5)	0.0029 (4)
C2	0.0291 (6)	0.0187 (5)	0.0291 (6)	0.0045 (4)	0.0177 (5)	0.0032 (4)
C3	0.0197 (5)	0.0141 (5)	0.0199 (5)	0.0019 (4)	0.0056 (4)	−0.0019 (4)
C4	0.0205 (6)	0.0209 (6)	0.0404 (7)	0.0008 (4)	0.0125 (5)	−0.0048 (5)
C5	0.0177 (5)	0.0197 (5)	0.0261 (5)	0.0011 (4)	0.0086 (4)	−0.0014 (4)
C6	0.0379 (7)	0.0274 (6)	0.0236 (6)	0.0089 (5)	0.0087 (5)	0.0031 (4)
C7	0.0281 (6)	0.0199 (6)	0.0407 (7)	0.0032 (5)	0.0133 (5)	−0.0032 (5)

C8	0.0289 (6)	0.0269 (6)	0.0340 (6)	0.0068 (5)	0.0097 (5)	0.0089 (5)
C9	0.0271 (6)	0.0319 (7)	0.0222 (5)	0.0042 (5)	0.0075 (4)	−0.0002 (5)

Geometric parameters (Å, º)

N1—C4	1.4963 (14)	C3—C1^{i}	1.5188 (15)
N1—C3	1.5033 (13)	C3—H3	1.0000
N1—H1A	0.891 (15)	C4—C5	1.5040 (16)
N1—H1B	0.876 (16)	C4—H4A	0.9900
N2—C6	1.3309 (17)	C4—H4B	0.9900
N2—C7	1.3319 (17)	C5—C9	1.3813 (17)
C1—C3^{i}	1.5188 (15)	C5—C6	1.3848 (16)
C1—C2	1.5283 (15)	C6—H6	0.9500
C1—H1C	0.9900	C7—C8	1.3750 (18)
C1—H1D	0.9900	C7—H7	0.9500
C2—C3	1.5193 (15)	C8—C9	1.3847 (18)
C2—H2A	0.9900	C8—H8	0.9500
C2—H2B	0.9900	C9—H9	0.9500
C4—N1—C3	113.56 (9)	C1^{i}—C3—H3	109.0
C4—N1—H1A	110.8 (9)	C2—C3—H3	109.0
C3—N1—H1A	109.0 (9)	N1—C4—C5	112.05 (9)
C4—N1—H1B	107.3 (10)	N1—C4—H4A	109.2
C3—N1—H1B	111.2 (10)	C5—C4—H4A	109.2
H1A—N1—H1B	104.6 (13)	N1—C4—H4B	109.2
C6—N2—C7	116.57 (11)	C5—C4—H4B	109.2
C3^{i}—C1—C2	110.35 (9)	H4A—C4—H4B	107.9
C3^{i}—C1—H1C	109.6	C9—C5—C6	117.55 (11)
C2—C1—H1C	109.6	C9—C5—C4	122.80 (11)
C3^{i}—C1—H1D	109.6	C6—C5—C4	119.62 (11)
C2—C1—H1D	109.6	N2—C6—C5	124.49 (12)
H1C—C1—H1D	108.1	N2—C6—H6	117.8
C3—C2—C1	110.35 (9)	C5—C6—H6	117.8
C3—C2—H2A	109.6	N2—C7—C8	123.82 (12)
C1—C2—H2A	109.6	N2—C7—H7	118.1
C3—C2—H2B	109.6	C8—C7—H7	118.1
C1—C2—H2B	109.6	C7—C8—C9	118.55 (11)
H2A—C2—H2B	108.1	C7—C8—H8	120.7
N1—C3—C1^{i}	108.79 (9)	C9—C8—H8	120.7
N1—C3—C2	110.50 (8)	C5—C9—C8	118.99 (11)
C1^{i}—C3—C2	110.60 (9)	C5—C9—H9	120.5
N1—C3—H3	109.0	C8—C9—H9	120.5
C3^{i}—C1—C2—C3	−57.46 (14)	C7—N2—C6—C5	−0.2 (2)
C4—N1—C3—C1^{i}	−172.97 (9)	C9—C5—C6—N2	−1.4 (2)
C4—N1—C3—C2	65.43 (12)	C4—C5—C6—N2	176.74 (13)
C1—C2—C3—N1	178.12 (9)	C6—N2—C7—C8	1.7 (2)
C1—C2—C3—C1^{i}	57.60 (14)	N2—C7—C8—C9	−1.5 (2)

C3—N1—C4—C5	179.29 (9)	C6—C5—C9—C8	1.50 (18)
N1—C4—C5—C9	−88.08 (14)	C4—C5—C9—C8	−176.57 (11)
N1—C4—C5—C6	93.89 (13)	C7—C8—C9—C5	−0.16 (19)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1	0.891 (15)	2.237 (15)	3.1215 (10)	171.7 (12)
N1—H1*B*···Cl1^{ii}	0.876 (16)	2.287 (16)	3.1588 (10)	173.8 (13)
C3—H3···Cl1^{iii}	1.00	2.76	3.7106 (11)	158
C8—H8···Cl1^{iv}	0.95	2.76	3.6020 (13)	148

Symmetry codes: (ii) $-x+1, -y, -z+1$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $x+1/2, -y-1/2, z+1/2$.