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Crystal structure of ammonium bis[(pyridin-2-yl)methyl]ammonium dichloride

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In the title molecular salt, $C_{12}H_{14}N_3^+ \cdot NH_4^+ \cdot 2Cl^-$, the central, secondary-amine, N atom is protonated. The bis[(pyridin-2-yl)methyl]ammonium and ammonium cations both lie across a twofold rotation axis. The dihedral angles between the planes of the pyridine rings is 68.43 (8)°. In the crystal, N—H⋯N and N—H⋯Cl hydrogen bonds link the components of the structure, forming a two-dimensional network parallel to (010). In addition, weak C—H⋯Cl hydrogen bonds exist within the two-dimensional network.

1. Related literature

For background to atom-transfer radical addition reactions, see: Eckenhoff & Pintauer (2010); Kharasch *et al.* (1945); Iqbal *et al.* (1994); Braunecker & Matyjaszewski (2007); Matyjaszewski *et al.* (2001); Tang *et al.* (2008). For the synthesis, see: Carvalho *et al.* (2006). For related structures, see: Junk *et al.* (2006).
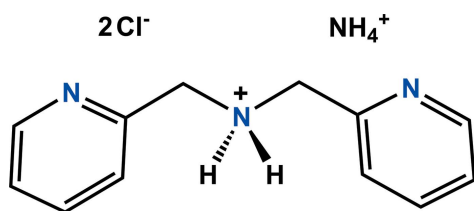
2. Experimental

2.1. Crystal data

$C_{12}H_{14}N_3^+ \cdot H_4N^+ \cdot 2(Cl^-)$	$V = 697.47$ (14) Å^3
$M_r = 289.20$	$Z = 2$
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation
$a = 8.895$ (1) Å	$\mu = 0.45$ mm^{-1}
$b = 17.676$ (2) Å	$T = 100$ K
$c = 4.4360$ (5) Å	$0.55 \times 0.30 \times 0.25$ mm

2.2. Data collection

Bruker APEXII CCD diffractometer	4292 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)	2126 independent reflections
$T_{min} = 0.605$, $T_{max} = 0.746$	2088 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.016$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	$\Delta\rho_{max} = 0.42$ e Å^{-3}
$wR(F^2) = 0.066$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
$S = 1.06$	Absolute structure: Flack x determined using 748 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
2126 reflections	
89 parameters	
1 restraint	
H atoms treated by a mixture of independent and constrained refinement	Absolute structure parameter: 0.04 (2)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1B⋯Cl1^i	0.99	2.80	3.7145 (15)	154
C6—H6⋯Cl1^{ii}	0.95	2.75	3.6410 (15)	157
N1—H1C⋯Cl1^{iii}	0.91	2.23	3.1239 (9)	168
N1—H1D⋯Cl1^{iv}	0.91	2.23	3.1239 (9)	168
N4—H4A⋯N2	0.90 (2)	2.09 (2)	2.9748 (15)	167 (2)
N4—H4B⋯Cl1	0.93 (2)	2.32 (2)	3.2362 (12)	170 (2)

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

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015) and *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Crystal structure of ammonium bis[(pyridin-2-yl)methyl]ammonium dichloride

Aaron Trischler, Kayode Oshin and Tomislav Pintauer

S1. Chemical context

Atom transfer Radical Addition (ATRA) reactions involve the formation of carbon-carbon bonds through the addition of saturated poly-halogenated hydrocarbons to alkenes (Eckenhoff & Pintauer, 2010). First reported by Kharasch in the 1940s (Kharasch *et al.*, 1945), the reaction incorporates halogen group functionalities within products; which can then be used as starting reagents in further functionalization reactions (Iqbal *et al.*, 1994). Subsequently, ATRA has emerged as some of the most atom economical methods for simultaneously forming C–C and C–X bonds; leading to the production of more attractive molecules with well-defined compositions, architectures, and functionalities (Braunecker & Matyjaszewski , 2007). Structural studies suggest that the type of ligand used in atom transfer radical reactions significantly influence the behavior of catalyst generated due to different steric and electronic interactions with the metal center (Matyjaszewski *et al.*, 2001). Copper complexes made with tetradentate nitrogen-based ligands such as 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane (Me$_6$CYCLAM), *tris*(2-pyridylmethyl)amine (TPMA), *tris*(2-(dimethyl-amino)ethyl)amine (Me$_6$TREN), and *bis*(2-pyridylmethyl) amine (BPMA) are currently some of the most active multidentate structures used in atom transfer radical reactions (Tang *et al.*, 2008). Given the significance of these ligands, we present the crystal structure of a protonated *bis*(2-pyridylmethyl)amine (BPMA) salt.

S2. Structural commentary

The molecular structure of the title compound is shown in Fig 1. The bis[(pyridin-2-yl)methyl]ammonium and ammonium cations both lie across a twofold rotation axis. The dihedral angles between the pyridine rings is 68.43 (8)°. This is in contrast to the values of the dihedral anlges in bis(2-pyridylmethyl)ammonium bromide and bis(2-pyridyl-methyl)ammonium iodide (Junk *et al.*, 2006) which are 38.47 (13) and 5.17 (9)°, respectively. In the crystal, N—H⋯N and N—H⋯Cl hydrogen bonds link the components of the structure forming a two-dimensional network parallel to (010) (Fig. 2). In addition, weak C—H⋯Cl hydrogen bonds exist within the two-dimensional network.

S3. Synthesis and crystallization

***Bis*(2-pyridylmethyl)amine salt** (BPMA) was synthesized and purified following literature procedures (Carvalho *et al.*, 2006) and the reaction scheme is shown in Fig. 3. A 500 mL round bottom flask was filled with 100 mL of methanol then 2-pyridinecarboxaldehyde (8.90 mL, 94.0 mmol) added. The flask was placed in an ice bath to cool with the solution mixing. After 15 minutes, 2-pyridylmethylamine (9.70 mL, 94.0 mmol) was added to give a dull yellow colored solution. Flask was removed from ice bath and mixture allowed to react at room temperature for 1 hour to give a red colored solution. The flask was placed back in an ice bath and sodium borohydride (3.500 g, 94.0 mmol) was added in small amounts to prevent foaming. After this addition, the flask was removed from the ice bath and the mixture left to stir overnight. Concentrated hydrochloric acid was added to the mixture drop-wise until a pH of 4 was attained producing an orange mixture. An extraction was performed on the mixture in a separatory funnel with dichloromethane until the

organic phase became colorless. The aqueous phase was separated and its pH adjusted to 10 with Na_2CO_3. A second extraction was performed with dichloromethane on this mixture and the organic layer isolated and dried using $MgSO_4$. Solvent was removed to produce the desired ligand as a dark-brown colored oil (14.910 g, 80%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ3.48 (s, 1H), δ4.01 (s, 4H), δ7.14 (t, J = 7.6 Hz, 2H), δ 7.34 (d, J = 7.6 Hz, 2H), δ 7.63 (t, J = 7.6 Hz, 2H), δ 8.53 (d, J = 4.8 Hz, 2H). ^{13}C NMR (CDCl$_3$, 400 MHz): δ 156.67, 149.20, 136.74, 122.73, 122.48, 53.25. FT—IR (liquid) v (cm^{-1}): 3283 (b), 3003 (m), 2818 (b), 1587 (s), 1566 (m), 1471 (s), 1429 (s), 1356 (b). Colorless single crystals suitable for X-Ray analysis were obtained from slow cooling of BPMA ligand in the refrigerator.

S4. Refinement

All H atoms, except for those of the ammonium cation, were placed in calculated positions and refined in a riding-model approximation, with C—H = 0.95 - 0.99 Å, N—H = 0.91 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$. The two unique H atoms of the ammonium cation were refined indpendently with isotropic displacement parameters.
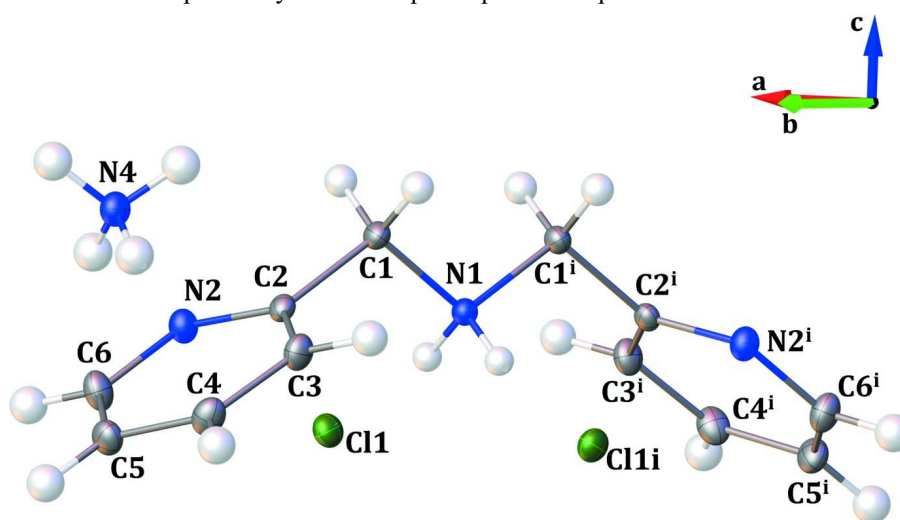

Figure 1

The molecular structure, shown with 50% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms [symmetry code: (i) -x+2, -y+2, z].
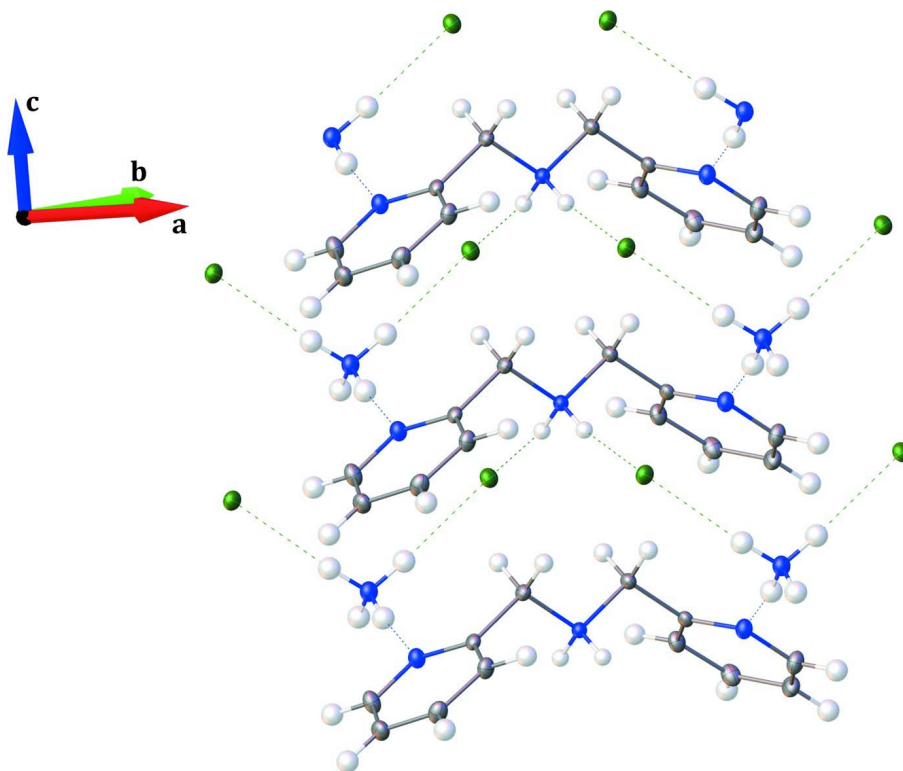
Figure 2

Part of the crystal structure with hydrogen bonds shown as dashed lines.

Ammonium bis[(pyridin-2-yl)methyl]ammonium dichloride

Crystal data

$C_{12}H_{14}N_3^+ \cdot H_4N^+ \cdot 2(Cl^-)$	$D_x = 1.377$ Mg m^{-3}
$M_r = 289.20$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $P2_12_12$	Cell parameters from 3559 reflections
$a = 8.895$ (1) Å	$\theta = 2.3–31.8°$
$b = 17.676$ (2) Å	$\mu = 0.45$ mm^{-1}
$c = 4.4360$ (5) Å	$T = 100$ K
$V = 697.47$ (14) Å^3	Rod, colourless
$Z = 2$	$0.55 \times 0.30 \times 0.25$ mm
$F(000) = 304$	

Data collection

Bruker APEXII CCD diffractometer	4292 measured reflections
Radiation source: fine focus sealed tube	2126 independent reflections
Graphite monochromator	2088 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.016$
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)	$\theta_{max} = 31.9°$, $\theta_{min} = 2.6°$
	$h = -12 \rightarrow 12$
$T_{min} = 0.605$, $T_{max} = 0.746$	$k = -25 \rightarrow 20$
	$l = -6 \rightarrow 5$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.025$	and constrained refinement
$wR(F^2) = 0.066$	$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 0.1504P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2126 reflections	$(\Delta/\sigma)_{max} = 0.001$
89 parameters	$\Delta\rho_{max} = 0.42$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.17$ e Å^{-3}
Primary atom site location: structure-invariant	Absolute structure: Flack x determined using
direct methods	748 quotients [(I^+)-(I^-)]/[(I^+)+(I^-)] (Parsons *et al.*,
Secondary atom site location: difference Fourier	2013)
map	Absolute structure parameter: 0.04 (2)

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.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.92866 (15)	0.93964 (7)	1.2090 (3)	0.0121 (2)	
H1A	0.8529	0.9629	1.3436	0.015*	
H1B	1.0064	0.9156	1.3367	0.015*	
C2	0.85420 (16)	0.88021 (7)	1.0170 (3)	0.0110 (2)	
C3	0.93696 (16)	0.81886 (8)	0.9096 (4)	0.0149 (3)	
H3	1.0412	0.8146	0.9525	0.018*	
C4	0.86432 (17)	0.76416 (8)	0.7391 (4)	0.0169 (3)	
H4	0.9174	0.7210	0.6683	0.020*	
C5	0.71328 (17)	0.77338 (8)	0.6736 (4)	0.0164 (3)	
H5	0.6615	0.7375	0.5526	0.020*	
C6	0.63891 (16)	0.83632 (8)	0.7888 (4)	0.0168 (3)	
H6	0.5351	0.8424	0.7442	0.020*	
N1	1.0000	1.0000	1.0188 (4)	0.0103 (3)	
H1C	1.0711	0.9787	0.8982	0.012*	0.5
H1D	0.9289	1.0213	0.8982	0.012*	0.5
N2	0.70678 (14)	0.88881 (7)	0.9597 (3)	0.0134 (2)	
Cl1	0.73444 (4)	1.08251 (2)	1.69586 (8)	0.01425 (9)	
N4	0.5000	1.0000	1.2452 (4)	0.0142 (3)	
H4A	0.558 (2)	0.9696 (11)	1.131 (5)	0.021*	
H4B	0.563 (2)	1.0295 (11)	1.363 (5)	0.021*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0123 (5)	0.0129 (5)	0.0112 (5)	−0.0025 (4)	0.0005 (5)	0.0010 (5)
C2	0.0108 (6)	0.0111 (5)	0.0111 (5)	−0.0015 (4)	0.0004 (5)	0.0024 (5)
C3	0.0109 (6)	0.0145 (6)	0.0194 (6)	0.0008 (5)	0.0020 (5)	−0.0002 (5)

C4	0.0163 (6)	0.0136 (5)	0.0208 (7)	0.0005 (5)	0.0044 (6)	−0.0024 (5)
C5	0.0165 (6)	0.0151 (5)	0.0176 (6)	−0.0034 (5)	−0.0001 (6)	−0.0038 (5)
C6	0.0126 (6)	0.0152 (6)	0.0225 (7)	−0.0001 (5)	−0.0036 (6)	−0.0016 (6)
N1	0.0099 (7)	0.0105 (6)	0.0104 (7)	−0.0006 (6)	0.000	0.000
N2	0.0118 (5)	0.0118 (4)	0.0167 (6)	0.0002 (4)	−0.0006 (4)	−0.0007 (4)
Cl1	0.01141 (14)	0.01526 (14)	0.01608 (15)	0.00146 (10)	−0.00198 (11)	0.00017 (11)
N4	0.0120 (7)	0.0136 (7)	0.0170 (9)	0.0008 (6)	0.000	0.000

Geometric parameters (Å, º)

C1—N1	1.5010 (16)	C5—C6	1.392 (2)
C1—C2	1.5060 (19)	C5—H5	0.9500
C1—H1A	0.9900	C6—N2	1.3418 (19)
C1—H1B	0.9900	C6—H6	0.9500
C2—N2	1.3442 (18)	N1—C1^i	1.5010 (16)
C2—C3	1.3944 (19)	N1—H1C	0.9100
C3—C4	1.387 (2)	N1—H1D	0.9100
C3—H3	0.9500	N4—H4A	0.898 (18)
C4—C5	1.384 (2)	N4—H4B	0.926 (18)
C4—H4	0.9500		
N1—C1—C2	111.33 (12)	C4—C5—C6	118.59 (14)
N1—C1—H1A	109.4	C4—C5—H5	120.7
C2—C1—H1A	109.4	C6—C5—H5	120.7
N1—C1—H1B	109.4	N2—C6—C5	123.12 (13)
C2—C1—H1B	109.4	N2—C6—H6	118.4
H1A—C1—H1B	108.0	C5—C6—H6	118.4
N2—C2—C3	122.57 (13)	C1^i—N1—C1	111.59 (15)
N2—C2—C1	117.19 (12)	C1^i—N1—H1C	109.3
C3—C2—C1	120.23 (12)	C1—N1—H1C	109.3
C4—C3—C2	118.84 (13)	C1^i—N1—H1D	109.3
C4—C3—H3	120.6	C1—N1—H1D	109.3
C2—C3—H3	120.6	H1C—N1—H1D	108.0
C5—C4—C3	118.98 (13)	C6—N2—C2	117.87 (12)
C5—C4—H4	120.5	H4A—N4—H4B	108.0 (19)
C3—C4—H4	120.5		
N1—C1—C2—N2	−94.13 (14)	C4—C5—C6—N2	0.3 (2)
N1—C1—C2—C3	86.76 (15)	C2—C1—N1—C1^i	178.68 (13)
N2—C2—C3—C4	−0.5 (2)	C5—C6—N2—C2	1.1 (2)
C1—C2—C3—C4	178.53 (13)	C3—C2—N2—C6	−0.9 (2)
C2—C3—C4—C5	1.9 (2)	C1—C2—N2—C6	179.97 (13)
C3—C4—C5—C6	−1.7 (2)		

Symmetry code: (i) −*x*+2, −*y*+2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···Cl1[i]	0.99	2.80	3.7145 (15)	154
C6—H6···Cl1[ii]	0.95	2.75	3.6410 (15)	157
N1—H1C···Cl1[iii]	0.91	2.23	3.1239 (9)	168
N1—H1D···Cl1[iv]	0.91	2.23	3.1239 (9)	168
N4—H4A···N2	0.90 (2)	2.09 (2)	2.9748 (15)	167 (2)
N4—H4B···Cl1	0.93 (2)	2.32 (2)	3.2362 (12)	170 (2)

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