

2,2'-(Iminodimethylene)bis(1*H*-benzimidazolium)(1+) chlorideSheng-Run Zheng,^a Yue-Peng Cai,^b Xue-Li Zhang^a and Cheng-Yong Su^{a*}^aSchool of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and ^bDepartment of Chemistry, South China Normal University, Guangzhou 510631, People's Republic of China
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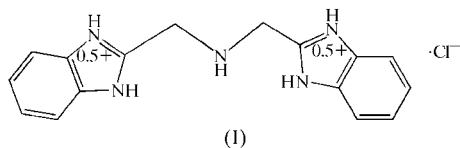
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The title compound, $C_{16}H_{16}N_5^+Cl^-$ ($nbbH^+Cl^-$), displays $N-H\cdots N$, $N-H\cdots Cl$ and $\pi-\pi$ interactions in the crystal packing. The Cl^- anion is chelated by the $nbbH^+$ cation *via* two $N-H\cdots Cl$ hydrogen bonds. Inter-ion $N-H\cdots N$ and $N-H\cdots Cl$ hydrogen bonds link ions related by 2_1 screw axes into chains along the *c* axis. These chains are further linked by glide-plane operations to generate a three-dimensional network, which is additionally stabilized by interchain $\pi-\pi$ interactions.

Comment

Bis(benzimidazol-2-ylmethyl)amine (*nbb*) has been utilized extensively to synthesize various transition metal complexes (Wahnon *et al.*, 1994; Berends & Stephan, 1984). Each benzimidazole arm of *nbb* possesses one imine N atom and one amine NH group. The two imine N atoms can act as coordination donors to chelate a metal ion, while the two amine NH groups are potential hydrogen-bond donors. Without metal coordination, the two imine N atoms can also behave as hydrogen-bond acceptors. Therefore, *nbb* is a good candidate for the formation of hydrogen-bonded adducts *via* intermolecular interactions. We have been interested in the assembly of supramolecular aggregates with benzimidazole-related compounds (Su *et al.*, 1998, 2000; Zhang *et al.*, 2005) and report here the structure of the title compound, $nbbH^+Cl^-$, (I). The single-crystal structure of *nbb* has been



reported previously both at room temperature (Calderazzo *et al.*, 2003) and at 150 K (Tarazon Navarro & McKee, 2003); in both reports, the *nbb* molecule is disordered about an inversion centre.

Our analysis establishes that the title compound has partial protonation of the two imine N atoms, as shown in Fig. 1. The $nbbH^+$ cation adopts an almost planar conformation, the two benzimidazole systems forming a dihedral angle of $5.36(9)^\circ$. Occupancy refinement showed that the H atom involved in ring protonation is equally disordered over the N2 and N3 sites, and each five-membered ring possesses a half-positive-charge, giving rise to the overall $nbbH^+$ cation (see scheme). The dimensions of the five-membered rings are fully consistent with this assignment. As listed in Table 1, the geometry of each benzimidazole ring is the same; in particular, the N2—C2 bond distance is identical to the N3—C10 distance [mean = $1.315(3) \text{ \AA}$], while the N1—C2 and N4—C10 distances are also not significantly different [mean = $1.335(3) \text{ \AA}$]. These findings are consistent with the N2—C2 and N3—C10 bonds possessing more double-bond character than the N1—C2 and N3—C10 bonds. In the disordered non-protonated *nbb* parent molecule at low temperature, the $N=C$ distance is $1.3183(17) \text{ \AA}$ and the $C-N(H)$ distance is $1.3573(17) \text{ \AA}$ (Tarazon Navarro & McKee, 2003).

All five N atoms of the $nbbH^+$ ion are involved in hydrogen bonds, as shown in Table 2. The Cl^- anion is chelated by atoms N1 and N4 *via* $N-H\cdots Cl$ hydrogen bonds. Atoms N2 and N3 form mutual inter-ion $N2-H\cdots N3$ and $N3-H\cdots N2$ hydrogen bonds (as shown in Fig. 2), each H atom having an occupancy of 0.5. Since the $nbbH^+$ cation is bent, with two methylene (CH_2) groups protruding between the two planar

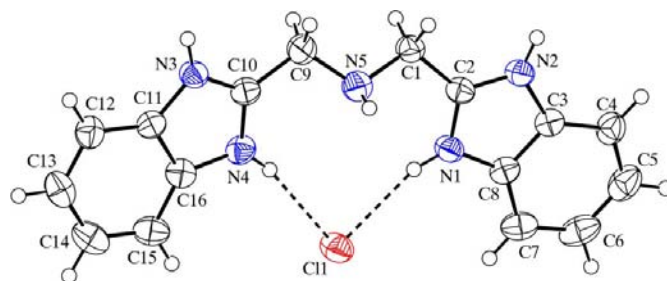


Figure 1

A view of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Dashed lines indicate intramolecular hydrogen bonds.

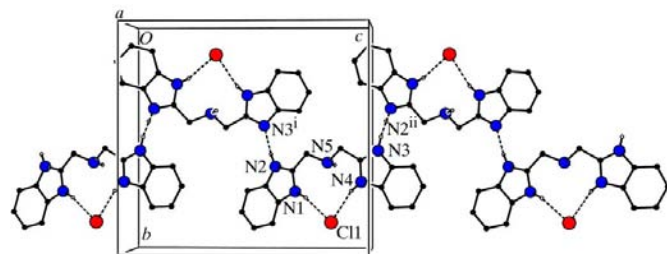


Figure 2

A view showing the hydrogen-bonded chains along the *c* axis. Dashed lines indicate hydrogen bonds and C-bound H atoms have been omitted. Symmetry codes are as given in Table 2.

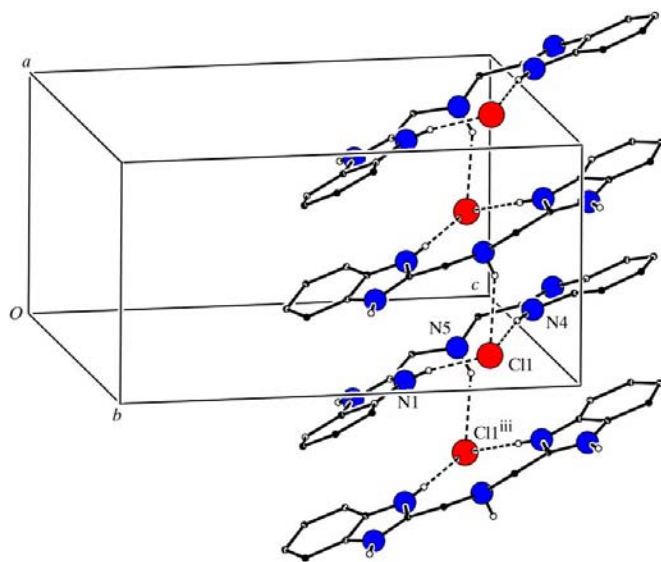


Figure 3

A view showing the hydrogen-bonded chain extending along the *a* axis; see Table 2 for details of the symmetry code. Dashed lines indicate hydrogen bonds and C-bound H atoms have been omitted. This plot also shows the π - π stacking between five- and six-membered rings in the sequence (bottom to top) $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$, (x, y, z) , $(\frac{1}{2} + x, \frac{3}{2} - y, z)$, $(1 + x, y, z)$.

benzimidazole rings, the ions are not assembled into a dimer by formation of two complementary N—H \cdots N hydrogen bonds. Instead, groups related by a 2_1 screw axis are connected in a head-to-tail fashion into an undulating one-dimensional chain, which extends along the *c* axis (Fig. 2). The N5—H5 moiety is also involved in a further N5—H5 \cdots Cl hydrogen bond (weaker than those of the chelating N—H \cdots Cl hydrogen bonds), which links ions related by an *a* glide into columnar one-dimensional chains extending along the *a* axis, as shown in Fig. 3. This chain can also be considered to consist of oppositely overlapped nbbH $^+$ cations. These cations are stacked along the *a* direction, with overlap between five- and six-membered rings in the sequence $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$, (x, y, z) , $(\frac{1}{2} + x, \frac{3}{2} - y, z)$, $(1 + x, y, z)$, etc. There exist π - π interactions between neighbouring cations, the shortest centroid-to-centroid distance being 3.554 (2) Å (Chen *et al.*, 2003). The N—H \cdots Cl hydrogen-bonded chain along the *a* axis is thus further stabilized by π - π stacking interactions. These chains along the *a* and *c* axial directions are also linked by N—H \cdots N hydrogen bonds by operation of the space group *n* glide to generate a three-dimensional network. Thus, the crystal packing is ordered *via* synergetic contributions from N—H \cdots N and N—H \cdots Cl hydrogen bonds and π - π interactions, which together assemble the cations and anions into a three-dimensional framework.

Experimental

The title compound was prepared by the condensation of imino-diacetic acid and 1,2-diaminobenzene in a 4 *N* HCl solution (yield 76%). Single crystals suitable for X-ray analysis were obtained by slow evaporation from an ethanol solution at room temperature.

Crystal data

$C_{16}H_{16}N_5^+ \cdot Cl^-$
 $M_r = 313.79$
 Orthorhombic, *Pna* 2_1
 $a = 7.607$ (2) Å
 $b = 13.615$ (3) Å
 $c = 14.544$ (3) Å
 $V = 1506.3$ (6) Å 3
 $Z = 4$
 $D_x = 1.384$ Mg m $^{-3}$

Data collection

Bruker SMART 1K CCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Siemens, 1996)
 $T_{min} = 0.757$, $T_{max} = 1.000$
 6569 measured reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.067$
 $S = 1.01$
 2020 reflections
 200 parameters
 H-atom parameters constrained

Mo $K\alpha$ radiation
 Cell parameters from 1785
 reflections
 $\theta = 2.1$ – 24.6°
 $\mu = 0.26$ mm $^{-1}$
 $T = 293$ (2) K
 Block, colourless
 $0.19 \times 0.04 \times 0.03$ mm

2020 independent reflections
 1771 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$
 $\theta_{max} = 25.0^\circ$
 $h = -8 \rightarrow 9$
 $k = -14 \rightarrow 16$
 $l = -8 \rightarrow 17$

$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.19$ e Å $^{-3}$
 $\Delta\rho_{min} = -0.16$ e Å $^{-3}$
 Absolute structure: Flack (1983),
 637 Friedel pairs
 Flack parameter: 0.36 (7)

Table 1

Selected interatomic distances (Å).

N1—C2	1.334 (3)	N3—C11	1.390 (3)
N1—C8	1.382 (3)	N4—C10	1.336 (3)
N2—C2	1.315 (3)	N4—C16	1.388 (3)
N2—C3	1.395 (3)	N5—C9	1.436 (3)
N3—C10	1.315 (3)	N5—C1	1.444 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> —H⋯ <i>A</i>
N1—H1 \cdots C11	0.86	2.31	3.146 (2)	164
N2—H2 \cdots N3 i	0.86	1.89	2.739 (2)	172
N3—H3 \cdots N2 ii	0.86	1.91	2.739 (2)	161
N4—H4 \cdots C11	0.86	2.41	3.247 (2)	166
N5—H5 \cdots Cl1 iii	0.90	2.52	3.306 (3)	147

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

The systematic absences allow the space group to be either *Pnma* or *Pna* 2_1 , but a sensible solution and refinement were only possible in *Pna* 2_1 . All H atoms were located in a difference Fourier map. It was obvious from the difference maps that protonation had occurred equally at atoms N2 and N3, and the H atoms at these sites were assigned an occupancy of 0.5. Atom H5 (at N5) was clearly located such that N5 had pyramidal geometry. All H atoms were then allowed for as riding atoms (C—H = 0.93 and 0.97 Å, and N—H = 0.86 and 0.90 Å), with $U_{iso}(H)$ values of 1.2 times $U_{eq}(C, N)$. Friedel pairs were measured; however, the Flack (1983) parameter was indeterminate, indicating probable inversion twinning.

Data collection: SMART (Siemens, 1993); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1062). Services for accessing these data are described at the back of the journal.

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