

2-(2-Pyridylamino)pyridinium nitrate mono-hydrate: two-dimensional supramolecular aggregation through hydrogen-bonding and π - π stacking interactions

Miao Du* and Xiao-Jun Zhao

College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, People's Republic of China

Correspondence e-mail: dumiao@public.tpt.tj.cn

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$

R factor = 0.068

wR factor = 0.182

Data-to-parameter ratio = 12.5

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

In the crystal structure of the title compound, $\text{C}_{10}\text{H}_{10}\text{N}_3^+\cdot\text{NO}_3^-\cdot\text{H}_2\text{O}$, (I), the asymmetric unit contains two crystallographically independent but similar subunits. The protonated $\text{C}_{10}\text{H}_{10}\text{N}_3^+$ cation adopts the normal *trans-trans* configuration and approximately planar geometry. Multiple hydrogen-bonding interactions expand the structure, resulting in a two-dimensional layered architecture, which is further stabilized by aromatic π - π stacking interactions between the protonated cations.

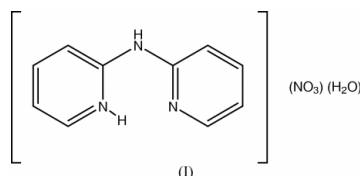
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Comment

Bis(2-pyridyl)amine has attracted great interest with regard to the spectra, magnetism and structural geometries of its metal complexes (Cotton *et al.*, 1997; Du & Zhao, 2004*a*). On the other hand, it is well known that aromatic compounds of this type also exhibit interesting proton-sponge properties (Du & Zhao, 2004*b*), *i.e.* species which can act as external proton acceptors through the formation of $\text{N}-\text{H}\cdots\text{Y}$ (where Y = acceptor species) hydrogen bonds. Here, we report the molecular and supramolecular structure of the title protonated nitrate of bis(2-pyridyl)amine, (I).



The crystal structure of (I) consists of two crystallographically independent but similar $\text{C}_{10}\text{H}_{10}\text{N}_3^+\cdot\text{NO}_3^-\cdot\text{H}_2\text{O}$ subunits in the asymmetric unit, as shown in Fig. 1. Both the mono-protonated cations *A* (referring to the cation containing the $\text{N}2-\text{H}2$ group) and *B* (referring to the cation containing the $\text{N}5-\text{H}5$ group) adopt the normal *trans-trans* configuration; all non-H atoms within each cation are almost coplanar and the r.m.s. deviations from the mean planes are 0.056 (4)

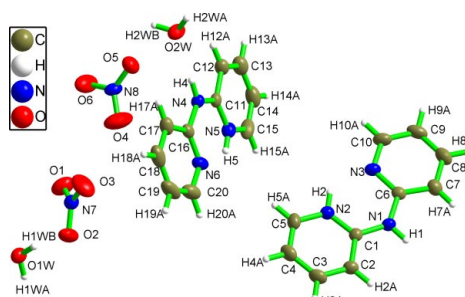


Figure 1

View of the asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level.

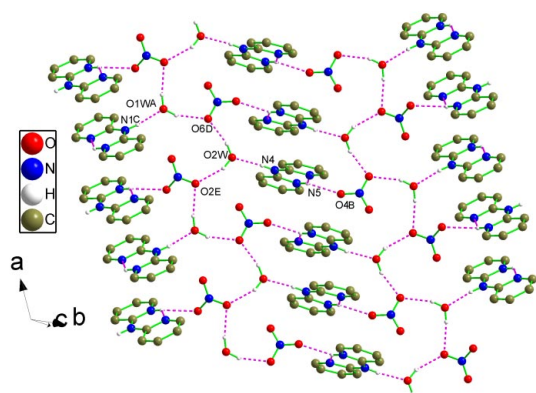


Figure 2

A view of the two-dimensional supramolecular architecture involving hydrogen-bonding (shown as dashed lines) and π - π stacking interactions. Atoms with suffixes *A*, *B*, *C*, *D* and *E* are related by the symmetry operators $(1+x, y-1, z)$, $(1-x, 1-y, 1-z)$, $(x, y-1, z-1)$, $(1+x, y, z)$ and $(x, y-1, z)$, respectively.

and 0.034 (5) Å, respectively. The dihedral angles between the pyridinio and pyridyl rings in *A* and *B* are 5.5 (4) and 3.5 (3)°, respectively. Selected bond lengths and angles are listed in Table 1.

Analysis of the crystal packing of the title compound shows the existence of three types of hydrogen-bonding interactions (N—H...N, N—H...O and O—H...O), which connect the cations, water molecules and nitrate anions to form a two-dimensional network. As depicted in Fig. 2, within the mono-protonated cations there are intramolecular N2—H2...N3 (for cation *A*) and N5—H5...N6 (for cation *B*) hydrogen bonds. In addition, each protonated N—H group also forms N2—H2...O1ⁱⁱ [symmetry code: (ii) $1-x, 1-y, 1-z$] (for cation *A*) or N5—H5...O4ⁱⁱ (for cation *B*) hydrogen bonds with the adjacent nitrate anion. The amide group is involved in an intermolecular N1—H1...O1wⁱ [symmetry code: (i) $1+x, y, 1+z$] (for cation *A*) or N4—H4...O2w (for cation *B*) hydrogen bond with the water molecule. Each water molecule also forms two O—H...O hydrogen-bonding interactions with the adjacent nitrate anions. Thus, the hydrogen-bonding interactions extend this structure into a two-dimensional supramolecular network (Fig. 2). The values for the hydrogen-bonding geometries (listed in Table 2) are in the normal ranges for such hydrogen-bonding interactions (Desiraju & Steiner, 1999). Furthermore, significant face-to-face π - π stacking interactions are observed between the parallel protonated cations, the closest separations being 3.534 (5) Å [center-to-center separation = 3.865 (5) Å] for cation *A* and 3.441 (4) Å [center-to-center separation = 3.624 (5) Å] for cation *B*, which further stabilize this network. Examination of this structure with PLATON (Spek, 2003) showed that there are no solvent-accessible voids in the crystal structure of (I).

Experimental

Reaction of bis(2-pyridyl)amine with Fe(NO₃)₂ (Lewis acid, acting as the proton-provided reagent here) in a 1:1 molar ratio in CH₃CN/CH₃OH afforded colorless block-shaped single crystals of (I) suitable for X-ray diffraction. Analysis calculated for the title compound: C

47.61, H 4.80, N 22.20%; found: C 47.84, H 4.59, N 22.16%. FT-IR data (KBr pellet, cm⁻¹): 3416 (*b*), 2959 (*w*), 1664 (*s*), 1603 (*s*), 1560 (*s*), 1507 (*m*), 1482 (*w*), 1454 (*s*), 1384 (*vs*), 1347 (*s*), 1268 (*w*), 1249 (*m*), 1197 (*w*), 1153 (*m*), 1121 (*w*), 1086 (*w*), 1043 (*w*), 1003 (*w*), 935 (*w*), 899 (*w*), 883 (*w*), 829 (*m*), 775 (*s*), 737 (*w*), 722 (*w*), 672 (*w*), 632 (*w*), 530 (*m*).

Crystal data

C₁₀H₁₀N₃⁺·NO₃⁻·H₂O
M_r = 252.24
 Triclinic, *P* $\bar{1}$
a = 7.795 (2) Å
b = 9.734 (3) Å
c = 17.164 (5) Å
 α = 95.982 (6)°
 β = 102.332 (6)°
 γ = 110.480 (5)°
V = 1168.9 (6) Å³

Z = 4
D_x = 1.433 Mg m⁻³
 Mo K α radiation
 Cell parameters from 845 reflections
 θ = 2.3–25.0°
 μ = 0.11 mm⁻¹
T = 293 (2) K
 Block, colorless
 0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan [SAINT (Bruker, 1998) and SADABS (Sheldrick, 1998)]
T_{min} = 0.967, *T_{max}* = 0.978
 4852 measured reflections

4088 independent reflections
 2266 reflections with *I* > 2 σ (*I*)
R_{int} = 0.018
 θ_{max} = 25.0°
h = -9 → 6
k = -10 → 11
l = -20 → 19

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.068
wR (*F*²) = 0.182
S = 1.10
 4088 reflections
 328 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.642P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.73 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.45 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.357 (4)	N4—C11	1.362 (4)
N1—C6	1.384 (4)	N4—C16	1.380 (4)
N2—C1	1.337 (4)	N5—C11	1.328 (4)
N2—C5	1.363 (4)	N5—C15	1.396 (5)
N3—C6	1.335 (4)	N6—C16	1.331 (5)
N3—C10	1.339 (5)	N6—C20	1.337 (5)
C1—N1—C6	129.6 (3)	C11—N4—C16	128.9 (3)
C1—N2—C5	122.1 (3)	C11—N5—C15	120.6 (4)
C6—N3—C10	117.1 (3)	C16—N6—C20	117.5 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1w ⁱ	0.86	1.92	2.775 (5)	173
N2—H2...N3	0.86	1.99	2.650 (5)	132
N2—H2...O1 ⁱⁱ	0.86	2.32	2.910 (4)	126
N4—H4...O2w	0.86	1.95	2.808 (4)	173
N5—H5...N6	0.86	2.00	2.651 (5)	131
N5—H5...O4 ⁱⁱ	0.86	2.22	2.827 (5)	127
O1w—H1wa...O6 ⁱⁱⁱ	0.90	2.01	2.857 (4)	157
O1w—H1wb...O2	0.89	2.03	2.908 (5)	169
O2w—H2wa...O6 ^{iv}	0.90	1.96	2.823 (4)	161
O2w—H2wb...O2 ^v	0.90	2.03	2.883 (4)	157

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

Although all H atoms were visible in difference maps, they were finally placed at calculated positions (0.93 Å for aromatic C–H, 0.86 Å for N–H and 0.89 Å for O–H) and refined in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C,N})$ and $1.5 U_{\text{eq}}(\text{O})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL97*.

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