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Key indicators

Single-crystal X-ray study

T = 298 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.042

wR factor = 0.110

Data-to-parameter ratio = 11.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2,3-Bis(2-pyridinio)-5,8-dimethoxyquinoxaline
dinitrate

In the crystal structure of the title compound, $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2^{2+} \cdot 2\text{NO}_3^-$, two pyridinium rings form dihedral angles of $48.0(2)$ and $33.3(4)^\circ$ with the mean quinoxaline plane, and a dihedral angle of $52.6(2)^\circ$ with each other. The orientation of the pyridinium rings is such that their N atoms face each other. Both pyridinium N—H groups participate in N—H \cdots O hydrogen bonds involving the O atoms of the nitrate anions. There exist significant π – π interactions responsible for the formation of the stacks along the *b* axis of the crystal.

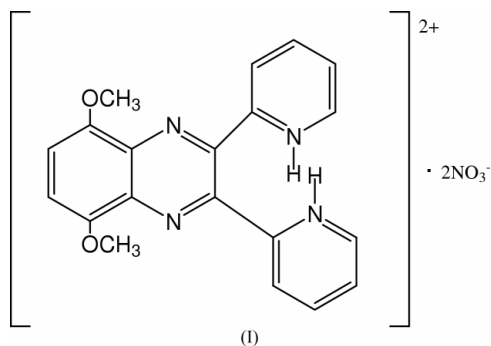
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Comment

2,3-Bis(2-pyridyl)quinoxaline and its derivatives represent an important class of chelating agents which have been extensively studied over the last two decades. Most of the studies focused on the electrochemical and photochemical properties of their metal complexes (Balzani *et al.*, 1996; Scott *et al.*, 1999). Aromatic compounds of this type also exhibit proton-sponge properties (Staab & Saupe, 1988; Robertson *et al.*, 1998), *i.e.* represent the species which can act as external proton acceptors through the formation of N—H \cdots Y hydrogen bonds. In the present paper, we report the crystal structure of the nitrate salt of diprotonated 2,3-bis(2-pyridyl)-5,8-dimethoxyquinoxaline (Bpdq), *i.e.* $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2^{2+} \cdot 2\text{NO}_3^-$, (I).



The cation of (I) consists of a quinoxaline ring system substituted with two protonated pyridine rings and two methoxy groups (Fig. 1). The pyridine rings cannot be coplanar with each other or with the quinoxaline system, as the planar conformation would cause sterically unacceptable contacts between the pyridyl *ortho*-H atoms. In fact, the existence of the adjacent pyridinium substituents causes substantial out-of-plane twist even within the quinoxaline itself, the torsion angle C2—C3—C12—C18 being $6.9(3)^\circ$; the mean atomic displacement from the least-squares quinoxaline plane is $0.0324(3) \text{ \AA}$. The pyridinium rings C12—C16/N3 and

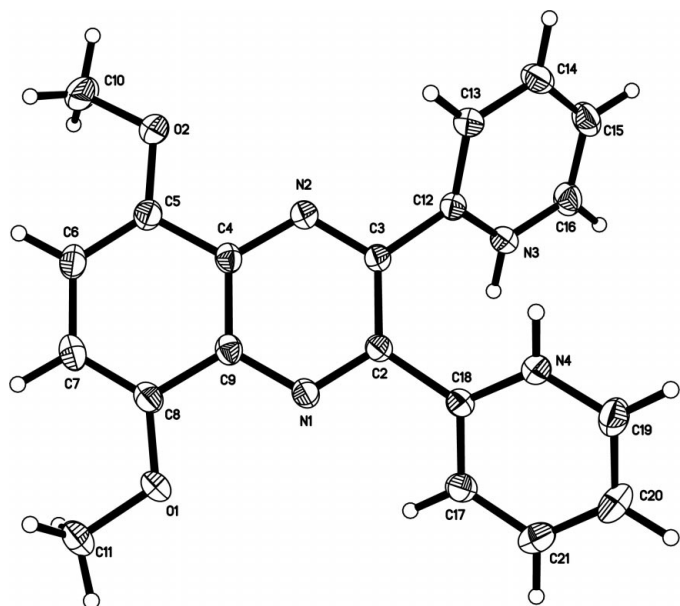


Figure 1
ORTEP (Johnson, 1976) view of diprotonated Bpdq shown with 30% probability ellipsoids.

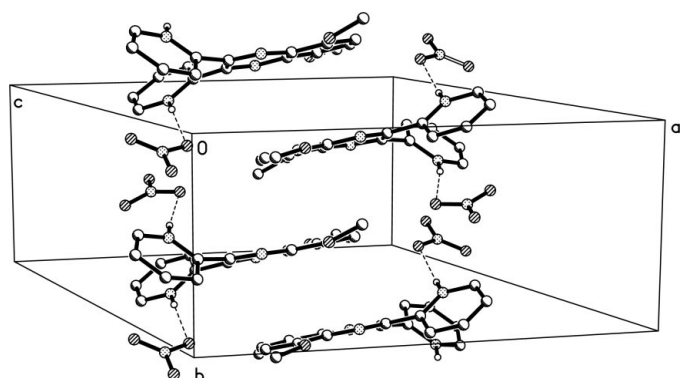


Figure 2
The packing diagram showing the cationic stacks in the crystal of (I).

C17–C21/N4 form dihedral angles of 48.0 (2) and 33.3 (4)°, respectively, with the mean quinoxaline plane, and a dihedral angle of 52.6 (2)° with each other. The orientation of the pyridinium rings is such that their N atoms face each other. These geometrical characteristics are similar to those observed in the structures of the analogues of (I) (Rasmussen *et al.*, 1990; Du *et al.*, 2001).

Selected bond distances and angles are given in Table 1. The C2–N1 and C3–N2 bond distances [1.313 (2) and 1.322 (2) Å, respectively] are noticeably shorter than N1–C9 and N2–C4 [1.355 (2) and 1.358 (2) Å, respectively], which is typical for quinoxaline system geometry (Anthony *et al.*, 1998; Rasmussen *et al.*, 1990). All N–C bond lengths are well within the range of values normally considered standard for single C–N and double C=N bonds [1.47 (Sasada, 1984) and 1.28 Å (Wang *et al.*, 1998), respectively].

Each pyridinium N–H group participates in N–H...O hydrogen bonds involving the nitrate O atom (Fig. 2 and Table 2). Furthermore, the neighbouring cations in the crystal of (I)

show substantial π – π -stacking interactions; the closest approach between the quinoxaline rings is about 3.5 Å, with the cationic stacks stretching along the *c* axis of the crystal.

Experimental

2,3-Bis(2-pyridyl)-5,8-dimethoxyquinoxaline (Bpdq) was prepared by the reaction of 1,4-dimethoxy-2,3-phenylenediamine (0.4 g, 2.4 mmol) and 2,2'-bipyridyl (0.5 g, 2.4 mmol) in ethanol (30 ml) at reflux for 4 h under argon, by a method similar to that reported in the literature (Waterland *et al.*, 1998). Orange single crystals of the title compound suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the acetonitrile solution of Bpdq in the presence of HNO₃.

Crystal data

C₂₀H₁₈N₄O₂²⁺·2NO₃⁻
M_r = 470.40
 Monoclinic, *P*2₁/*c*
a = 16.1380 (13) Å
b = 7.2682 (6) Å
c = 18.0257 (15) Å
 β = 104.344 (2)°
V = 2048.4 (3) Å³
Z = 4

D_x = 1.525 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 7963 reflections
 θ = 1.3–25.0°
 μ = 0.12 mm⁻¹
T = 298 (2) K
 Prism, orange
 0.30 × 0.20 × 0.15 mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan [SAINT (Bruker, 1998) and SADABS (Sheldrick, 1997)]
T_{min} = 0.965, *T_{max}* = 0.982
 8042 measured reflections

3569 independent reflections
 2323 reflections with *I* > 2σ(*I*)
R_{int} = 0.040
 θ_{max} = 25.0°
h = -15 → 19
k = -7 → 8
l = -21 → 21
 Intensity decay: <1%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.110
S = 0.97
 3569 reflections
 309 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.01
 $\Delta\rho_{max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.17 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0151 (12)

Table 1

Selected geometric parameters (Å, °).

N1–C2	1.313 (2)	N3–C16	1.333 (2)
N1–C9	1.355 (2)	N4–C18	1.343 (2)
N2–C3	1.322 (2)	N4–C19	1.333 (3)
N2–C4	1.358 (2)	O1–C11	1.424 (2)
N3–C12	1.351 (3)	O2–C10	1.432 (3)
C2–N1–C9	118.07 (17)	C19–N4–C18	122.47 (18)
C3–N2–C4	118.35 (17)	C8–O1–C11	117.52 (18)
C16–N3–C12	122.51 (19)	C5–O2–C10	116.03 (16)

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>
N3–H3A...O7 ⁱ	0.86	1.92	2.762 (4)	166
N4–H4B...O3	0.86	1.82	2.617 (2)	153

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

H-atoms positions were calculated and included in subsequent refinement in the riding model approximation.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998).

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