

Bis[2-(2-pyridinio)ethyl]ammonium triperchlorate

Ray J. Butcher,* Yilma Gultneh
and A. Raza Khan

Department of Chemistry, Howard University,
Washington, DC 20059, USA

Correspondence e-mail:
butcher@harker.nrl.navy.mil

Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.113
Data-to-parameter ratio = 10.3

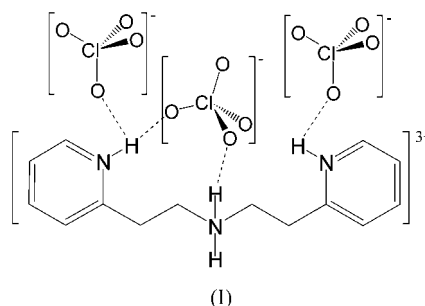
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{14}\text{H}_{20}\text{N}_3^{3+} \cdot 3\text{ClO}_4^-$, all three N atoms (one amine and two pyridyl) are protonated. At least one ClO_4^- ion is hydrogen bonded to each of the three N atoms. The H atom on the amine N atom shows the greatest distance to a ClO_4^- O atom (2.47 Å), while those on the two pyridyl N atoms are at distances ranging from 1.87 to 2.38 Å.

Received 26 July 2002
Accepted 20 September 2002
Online 5 October 2002

Comment

The tridentate ligand bis(2-pyridylethyl)amine (bpea) has been extensively used to synthesize transition metal complexes in modeling metalloenzyme active sites, due in part due to its similarity, in donor properties, to the biological donor histidyl imidazole. Two or more units have been linked to produce ligands with the possibilities of forming multinuclear complexes. Many groups (Butcher *et al.*, 2002) have used bpea as a chelating ligand for several metal ions, either as a single unit or as two or more units bridged by other moieties through the amine N atom. The amine N atom, which has a larger pK_a value (8.95) than those of the two pyridine N atoms (3.40 and 4.08) (Romary *et al.*, 1968), is protonated in the monoprotinated form of this ligand (Butcher *et al.*, 2002). On addition of three equivalents of acid, the triprotonated form, $\text{H}_3\text{bpea}^{3+}$, is isolated as the triperchlorate salt, (I). We report here the structure of (I).



The crystal structure shows that the amine and the two pyridyl N atoms are protonated, and each is hydrogen bonded to at least one perchlorate ion. The longest $\text{N}-\text{H} \cdots \text{O}_{\text{perchlorate}}$ distance (2.47 Å) observed is in a hydrogen bond involving the amine N atom, as expected on the basis of its greater pK_a value. This distance is shorter than that in the monoprotinated form of bpea (2.58 Å; Butcher *et al.*, 2002). In the monoprotinated form of this ligand, a closed conformation is observed, due to formation of intramolecular $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds involving the amine N atom and the unprotonated pyridine N atoms. In the case of the triprotonated form, this conformation is not possible, as the pyridine N atoms are protonated. Hence, the ligand adopts an open

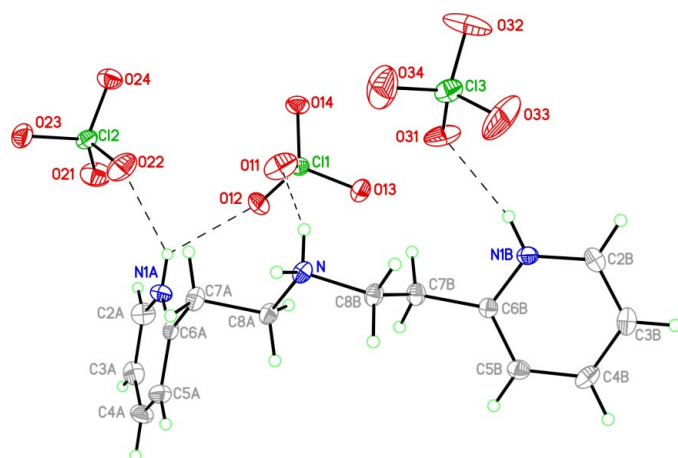


Figure 1

View of the molecule of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. For the disordered perchlorate anion, only the major component is shown.

conformation, with the formation of interionic hydrogen bonds with the perchlorate anions; the dihedral angle between the two pyridinium rings is $54.5(2)^\circ$.

Experimental

The free base is a light yellow oil, synthesized according to the literature method of Brady *et al.* (1961) and purified by vacuum distillation (b.p. 423 K/0.1 mm Hg). Addition of three equivalents of an aqueous solution of HClO_4 to a solution of the ligand in methanol and allowing the resulting solution to stand yielded crystals of the perchlorate salt of the triprotonated form of bis(2-ethylpyridine)-amine.

Crystal data

$\text{C}_{14}\text{H}_{20}\text{N}_3^{3+}\cdot 3\text{ClO}_4^-$	$Z = 2$
$M_r = 528.68$	$D_x = 1.620 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.6789(8) \text{ \AA}$	Cell parameters from 56 reflections
$b = 8.7858(10) \text{ \AA}$	$\theta = 4.8\text{--}13.2^\circ$
$c = 15.1139(15) \text{ \AA}$	$\mu = 0.49 \text{ mm}^{-1}$
$\alpha = 105.984(8)^\circ$	$T = 293(2) \text{ K}$
$\beta = 94.188(8)^\circ$	Plate, colorless
$\gamma = 99.581(9)^\circ$	$0.48 \times 0.24 \times 0.12 \text{ mm}$
$V = 1083.82(19) \text{ \AA}^3$	

Data collection

Siemens P4S diffractometer	$R_{\text{int}} = 0.015$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: refined from ΔF (SHELXTL; Sheldrick, 1997)	$h = 0 \rightarrow 10$
$T_{\text{min}} = 0.682$, $T_{\text{max}} = 0.909$	$k = -9 \rightarrow 9$
4007 measured reflections	$l = -17 \rightarrow 17$
3743 independent reflections	3 standard reflections
2885 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: 0.9%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.8913P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} = 0.027$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
3743 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
365 parameters	
H-atom parameters constrained	

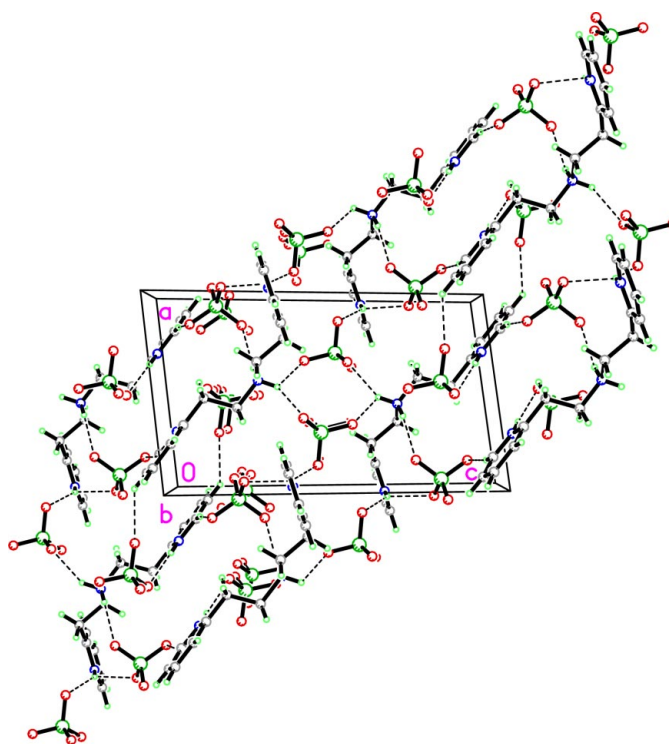


Figure 2

The molecular packing, viewed down the b axis. For the disordered perchlorate anion, only the major component is shown.

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{N1A--H1AA}\cdots\text{O22}$	0.86	2.19	2.916 (4)	142
$\text{N1A--H1AA}\cdots\text{O12}$	0.86	2.38	2.957 (3)	125
$\text{N1B--H1BA}\cdots\text{O31A}$	0.86	1.87	2.704 (9)	162
$\text{N1B--H1BA}\cdots\text{O31}$	0.86	2.07	2.915 (6)	166
$\text{N1B--H1BA}\cdots\text{O34B}$	0.86	2.27	3.09 (2)	157
$\text{N--H0A}\cdots\text{O24}^i$	0.90	2.10	2.912 (3)	150
$\text{N--H0A}\cdots\text{O23}^{ii}$	0.90	2.47	2.957 (3)	114
$\text{N--H0B}\cdots\text{O11}$	0.90	2.10	2.902 (3)	148

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

The disorder in one of the perchlorate anions (Cl3/O31--O34) was modeled by three tetrahedral sets of O atoms with occupancies of 0.510 (4), 0.358 (10), and 0.131 (10). All H atoms were fixed geometrically and allowed to ride on their parent atoms. The ammonium and pyridinium N–H bond distances were constrained to be 0.90 and 0.86 \AA , respectively.

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

RJB acknowledges the DoD for funds to upgrade the diffractometer. YG acknowledges the NIH-MBRS program for funding.

References

- Brady, L. E., Freifelder, M. & Stone, G. R. (1961). *J. Org. Chem.* **26**, 4757–4758.
- Butcher, R. J., Gultneh, Y. & Khan, A. R. (2002). *Acta Cryst.* **E58**, o1204–o1206.
- Romary, J. K., Zachariasen, R. D., Barger, J. D. & Schiesser, H. J. (1968). *J. Chem. Soc. C*, pp. 2884–2887.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison Wisconsin, USA.
- Siemens (1994). *XSCANS*. Version 2.10. Siemens Analytical X-ray Instruments Inc. Madison, Wisconsin, USA.