

## Structure of 2-[5-(2-Pyridyl)-1*H*-1,2,4-triazol-3-yl]pyridinium Perchlorate

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**Abstract.**  $C_{12}H_{10}N_5^+ \cdot ClO_4^-$ , monoclinic, space group  $C2/c$ ,  $Z = 8$ ,  $a = 32.889$  (6),  $b = 5.311$  (2),  $c = 15.712$  (4) Å,  $\beta = 104.95$  (2)°,  $D_x = 1.62$ ,  $D_m = 1.62$  (1) g cm<sup>-3</sup>. The structure consists of hydrogen-bonded ion pairs, with perchlorate to pyridinium (N–H) hydrogen bonds [ $N \cdots O = 2.795$  (5) Å]. There are additional hydrogen bonds between the triazole (N–H) group and a pyridine N atom in adjacent cations [ $N \cdots N = 3.006$  (5) Å]. The final  $R$  value is 0.042 ( $R_w = 0.041$ ) for 1286 observed reflections.

**Introduction.** Following the method described by Geldard & Lions (1965) 3,5-di(2-pyridyl)-1*H*-1,2,4-triazole was synthesized for use as a ligand in di- or polynuclear transition-metal complexes. The title compound crystallized from an ethanolic solution containing equimolar amounts of the triazole derivative and aqueous perchloric acid.

The structure determination was undertaken in order to investigate the planarity of the molecule, the orientation of the pyridine rings with respect to the triazole ring and the positions of the triazole proton, and the second protonated N atom.

The systematic absences  $h + k = 2n + 1$  for  $hkl$  and  $l = 2n + 1$  for  $h0l$  reflections indicated that the space group was  $Cc$  or  $C2/c$ . The choice of  $C2/c$  was justified by the successful solution of the structure. The intensities of 2056 independent reflections were measured ( $2^\circ < \theta < 24^\circ$ ) on an Enraf–Nonius CAD-4 automatic four-circle diffractometer [graphite-monochromated Mo  $K\alpha$  radiation;  $\lambda(\alpha_1) = 0.70930$  Å]. Data reduction was carried out in the usual way. No absorption corrections were applied ( $\mu = 3.1$  cm<sup>-1</sup>). Atomic scattering factors for neutral atoms with corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The structure was solved by direct methods using the program *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All following least-squares refinements and Fourier syntheses were based on the 1286 reflections with  $I > 2\sigma(I)$ . The function minimized was  $\sum (|F_o| - s|F_c|)^2$ . All H atoms were located in difference Fourier maps. The non-H atoms

Table 1. Atomic fractional positional coordinates ( $\times 10^4$ ) and isotropic thermal parameters

The atomic labelling of the H atoms refers to those of the C and N atoms to which they are bonded. E.s.d.'s are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}^*/B$ (Å <sup>2</sup> )
Cl(1)	5724.7 (4)	3493 (2)	1298 (1)	3.44 (3)
O(1)	5354 (1)	4876 (9)	1118 (4)	9.02 (20)
O(2)	5936 (2)	3892 (8)	604 (3)	6.94 (15)
O(3)	5645 (1)	875 (6)	1317 (3)	5.28 (12)
O(4)	6014 (1)	4271 (8)	2092 (3)	6.53 (14)
N(1)	3009 (1)	5297 (8)	526 (3)	3.17 (11)
N(2)	3404 (1)	4723 (8)	478 (3)	3.36 (11)
N(4)	3160 (1)	1794 (8)	1269 (2)	2.91 (10)
N(A)	4147 (1)	2186 (8)	615 (3)	3.37 (12)
N(B)	2202 (1)	5544 (8)	813 (3)	3.02 (11)
C(3)	3477 (1)	2609 (9)	935 (3)	2.87 (12)
C(5)	2867 (1)	3551 (9)	993 (3)	2.77 (11)
C(2A)	3878 (1)	1259 (9)	1064 (3)	2.84 (12)
C(3A)	4002 (2)	-719 (9)	1606 (3)	3.35 (14)
C(4A)	4396 (2)	-1739 (9)	1699 (3)	3.98 (15)
C(5A)	4662 (2)	-775 (11)	1238 (4)	4.22 (16)
C(6A)	4531 (2)	1240 (9)	688 (3)	3.84 (15)
C(2B)	2451 (1)	3614 (8)	1168 (3)	2.68 (11)
C(3B)	2333 (2)	1754 (9)	1675 (3)	3.22 (13)
C(4B)	1941 (2)	1888 (9)	1827 (3)	3.50 (14)
C(5B)	1681 (2)	3861 (9)	1485 (3)	3.46 (14)
C(6B)	1821 (2)	5615 (9)	988 (3)	3.47 (14)
H(1)	2879 (12)	6645 (83)	211 (27)	3.0
H(A)	4076 (13)	3384 (85)	283 (27)	3.0
H(3A)	3818 (12)	-1283 (81)	1290 (25)	3.0
H(4A)	4493 (12)	-3035 (83)	2126 (26)	3.0
H(5A)	4913 (12)	-1286 (83)	1273 (26)	3.0
H(6A)	4717 (12)	1987 (77)	328 (25)	3.0
H(3B)	2514 (12)	525 (83)	1903 (25)	3.0
H(4B)	1842 (12)	613 (81)	2165 (26)	3.0
H(5B)	1406 (12)	3963 (79)	1603 (25)	3.0
H(6B)	1669 (12)	6996 (83)	737 (25)	3.0

$$* B_{eq} = \frac{1}{3} \pi^2 \text{trace } \hat{U}.$$

were given anisotropic temperature factors. The positions of all H atoms were refined while their isotropic temperature factors were fixed at  $B = 3.0$  Å<sup>2</sup>. The conventional final residuals are  $R = 0.042$  and  $R_w = 0.041$  for the 1286 reflections used in the refinement and  $R = 0.078$ ,  $R_w = 0.066$  for all data. The atomic

positional and thermal parameters are listed in Table 1.\*

**Discussion.** The unit cell of the title compound contains eight symmetry-related  $C_{12}H_{10}N_5^+ \cdot ClO_4^-$  ion pairs. The  $ClO_4^-$  ion is hydrogen-bonded to a pyridinium N—H group of the protonated species  $C_{12}H_{10}N_5^+ |N-O = 2.795(5) \text{ \AA}; N-H \cdots O = 163(4)^\circ$ . The ion pair is shown in Fig. 1. Adjacent cations are weakly hydrogen bonded *via* a pyridine N and the triazole (N—H), with  $N(B)-N(1) = 3.006(5) \text{ \AA}$  and  $N(1)-H(1) \cdots N(B) = 153.9(4)^\circ$  (see Table 2).

The intramolecular bond lengths and angles listed in Table 2 are close to values reported earlier for triazole and pyridine structures (Goldstein, Ladell & Abowitz, 1969; Deuschl, 1965; Minshall & Sheldrick, 1978).

The  $C_{12}H_{10}N_5^+$  ion is nearly planar. The angle between the least-squares plane through the atoms in the triazole ring and that through the unprotonated pyridine ring is  $1.2(1)^\circ$  whereas the angle between the triazole ring and the pyridinium ring is  $7.7(1)^\circ$ .

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36970 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

E.s.d.'s are in parentheses. Superscripts indicate atoms whose coordinates are related to those in Table 1 by the following transformations: (i)  $1-x, 1-y, -z$ ; (ii)  $\frac{1}{2}-x, \frac{1}{2}-y, -z$ .

Cl(1)—O(1)	1.390 (4)	N(4)—C(2A)	1.350 (5)
Cl(1)—O(2)	1.452 (4)	N(4)—C(6A)	1.337 (6)
Cl(1)—O(3)	1.417 (4)	N(4)—H(4)	0.82 (4)
Cl(1)—O(4)	1.421 (4)	C(2A)—C(3A)	1.362 (6)
N(1)—N(2)	1.354 (5)	C(3A)—C(4A)	1.379 (6)
N(1)—C(5)	1.339 (5)	C(3A)—H(3A)	0.92 (4)
N(1)—H(1)	0.91 (4)	C(4A)—C(5A)	1.370 (7)
N(2)—C(3)	1.321 (6)	C(4A)—H(4A)	0.95 (4)
N(4)—C(3)	1.353 (5)	C(5A)—C(6A)	1.374 (7)
N(4)—C(5)	1.332 (5)	C(5A)—H(5A)	0.86 (4)
C(3)—C(2A)	1.460 (6)	C(6A)—H(6A)	1.01 (4)
C(5)—C(2B)	1.463 (6)		
N(B)—C(2B)	1.340 (5)	O(2)—N(A')	2.795 (5)
N(B)—C(6B)	1.352 (6)	O(2)—H(A')	2.00 (4)
C(2B)—C(3B)	1.386 (6)	N(B)—N(1')	3.006 (5)
C(3B)—C(4B)	1.374 (6)	N(B)—H(1')	2.16 (4)
C(3B)—H(3B)	0.89 (4)		
C(4B)—C(5B)	1.371 (6)	C(4A)—C(5A)—C(6A)	119.0 (5)
C(4B)—H(4B)	0.97 (4)	N(4)—C(6A)—C(5A)	118.9 (5)
C(5B)—C(6B)	1.369 (7)	C(2B)—N(B)—C(6B)	115.8 (4)
C(5B)—H(5B)	0.97 (4)	C(5)—C(2B)—C(3B)	120.3 (4)
C(6B)—H(6B)	0.92 (4)	C(5)—C(2B)—N(B)	116.1 (4)
N(2)—N(1)	110.6 (4)	N(B)—C(2B)—C(3B)	123.6 (4)
N(1)—N(2)—C(3)	101.7 (4)	C(2B)—C(3B)—C(4B)	118.5 (4)
C(3)—N(4)—C(5)	102.5 (4)	C(3B)—C(4B)—C(5B)	119.3 (5)
N(4)—C(3)—C(2A)	123.5 (4)	C(4B)—C(5B)—C(6B)	118.5 (4)
N(2)—C(3)—C(2A)	120.9 (4)	N(B)—C(6B)—C(5B)	124.3 (5)
N(2)—C(3)—N(4)	115.6 (4)	O(1)—Cl(1)—O(2)	109.7 (3)
N(1)—C(5)—N(4)	109.6 (4)	O(1)—Cl(1)—O(3)	111.4 (3)
N(1)—C(5)—C(2B)	124.2 (4)	O(1)—Cl(1)—O(4)	112.2 (3)
N(4)—C(5)—C(2B)	126.1 (4)	O(2)—Cl(1)—O(3)	106.6 (3)
C(2A)—N(4)—C(6A)	123.7 (4)	O(2)—Cl(1)—O(4)	105.9 (3)
C(3)—C(2A)—N(4)	116.8 (4)	O(3)—Cl(1)—O(4)	110.6 (3)
C(3)—C(2A)—C(3A)	125.1 (4)		
N(4)—C(2A)—C(3A)	118.1 (4)		
C(2A)—C(3A)—C(4A)	119.8 (5)		
C(3A)—C(4A)—C(5A)	120.5 (5)		

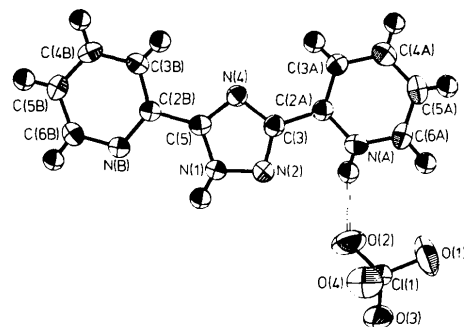


Fig. 1. The structure of  $C_{12}H_{10}N_5^+ \cdot ClO_4^-$ , showing the thermal vibration ellipsoids (probability 30%) of the atoms, and the atomic labelling. Hydrogen bonding between O(2) and H(4) is indicated by an open bond.

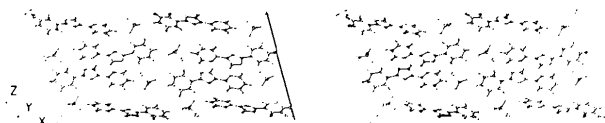


Fig. 2. The unit-cell packing of  $C_{12}H_{10}N_5^+ \cdot ClO_4^-$ .

The packing of the eight  $C_{12}H_{10}N_5^+ \cdot ClO_4^-$  ion pairs in the unit cell is shown in Fig. 2. The structure is obviously stabilized by van der Waals contacts between the  $C_{12}H_{10}N_5^+$  ions in the **b** and **c** directions. There are eight contact distances in the range of 3.33 (C—N) and 3.39  $\text{\AA}$  (C—C) to 3.54 (C—N) and 3.48  $\text{\AA}$  (C—C) between non-H ring atoms in adjacent cations.

Although the neutral ligand 3,5-di-(2-pyridyl)-1H-1,2,4-triazole may use four coordination sites [N(B), N(4), N(2) and N(A), see Fig. 1], preliminary experiments have shown that transition-metal complexes with the deprotonated ligand are isolated more easily. Coordination then takes place *via* the N atoms N(B), N(1), N(2) and N(A) forming dinuclear structures. The X-ray structure of a  $Cu^{II}$  compound of this ligand is under investigation (Prins, Birker, Verschoor, Haasnoot & Reedijk, 1982).

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## References

- DEUSCHL, H. (1965). *Ber. Bunsenges. Phys. Chem.* **69**, 550–560.
- GELDARD, J. F. & LIONS, F. (1965). *J. Org. Chem.* **30**, 318–319.
- GOLDSTEIN, P., LADELL, J. & ABOWITZ, G. (1969). *Acta Cryst.* **B25**, 135–143.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 103–151. Birmingham: Kynoch Press.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MINSHALL, P. C. & SHELDRIK, G. M. (1978). *Acta Cryst.* **B34**, 1378–1380.
- PRINS, R., BIRKER, P. J. M. W. L., VERSCHOOR, G. C., HAASNOOT, J. G. & REEDIJK, J. (1982). To be published.