Crystal structure of 4,4′-bipyridinium bis(hydrogen 3,5-pyrazole-dicarboxylate) tetrahydrate, $[C_5H_4N_2O_4]_2[C_{10}H_8N_2] \cdot 4H_2O$

Xiu-Ying Li, Ling Liu, Shan-Shan Wang, Miao-Miao Wang and Guang-Bo Che*

Department of Chemistry, Jilin Normal University, Siping 136000, Jilin, P. R. China

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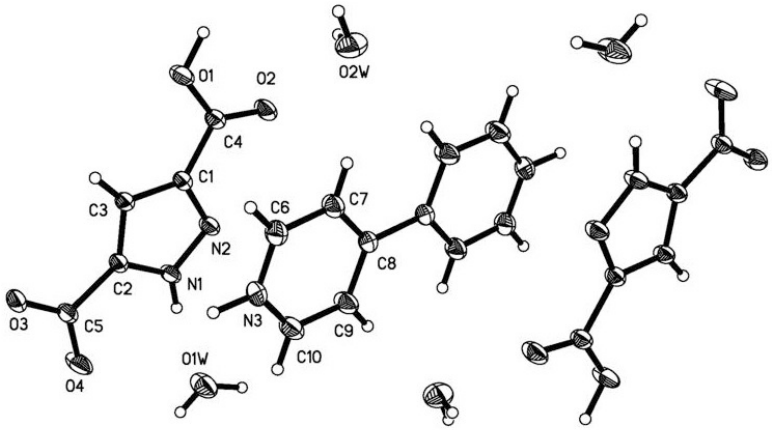

Abstract

$C_{20}H_{24}N_6O_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 7.1346(6) Å, b = 8.5912(8) Å, c = 11.0113(9) Å, α = 88.068(7)°, β = 71.416(8)°, γ = 68.866(8)°, V = 594.2 Å^3, Z = 1, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.095, T = 292 K.

Source of material

3,5-Pyrazoledicarboxylic acid (0.1741 g, 1 mmol) and 4,4′-bipyridine (0.0781 g, 0.5 mmol) were dissolved in distilled water (12 ml). The resulting solution was stirred for about 3 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 393 K for 3 d under autogenous pressure. The reaction system was then cooled slowly to room temperature. Colorless crystals suitable for X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature.

Experimental details

All H atoms on C atoms were positioned geometrically (d(C—H) = 0.93 Å) and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C). The hydrogen atoms of water molecules were located from difference Fourier maps and refined with U_{iso}(H) = 1.5 U_{eq}(O).

Discussion

In complicated compounds, weak intermolecular forces, such as hydrogen bonding, π–π stacking, dipole-dipole attractions and van der Waals interactions, have been studied in depth and can be used in the design of molecular solids with specific supramolecular structures and functions [1]. Thus, in the weak interactions, the study of hydrogen bonding is important for understanding the crystal structures [2-4]. So far, although an enormous amount of compounds showing hydrogen bonding leading to high-dimensional networks have been reported, such as 1D chains, 2D grids, 3D porous structures [5-6], to the best of our knowledge, no compounds based on 3,5-pyrazole-dicarboxylic acid and 4,4′-bipyridine which forms high-dimensional networks through hydrogen bonding have been reported.

To distinctly investigate the structures of frameworks, it would be important to explore the connection modes of organic ligands. The title structure contains a network of N–H···O, O–H···O and O–H···N hydrogen bonds, involving 3,5-pyrazoledicarboxylate anions, 4,4′-bipyridinium cations and free water molecules as hydrogen-bonding donors and acceptors, respectively. 3,5-Pyrazoledicarboxylate and free water molecule O1W are linked through four kinds of inter-hydrogen bonding [(1) d(O1W–H1WA···N2) = 2.888(2) Å; (2) d(O1W–H1WB···O2) = 3.002(2) Å; (3) d(O1–H1···O4) = 2.515(2) Å; (4) d(N1–H4···O1W) = 2.799(2) Å] into a chain along [010]. Further, the chains are connected by 4,4′-bipyridinium [(5) d(N3–H3···O3) = 2.628(2) Å] into a layer structure in the (011) plane. It is remarkable that a ladder structure is formed by chains and free water molecules O2W along [110] direction. The chains and O2W are linked by hydrogen bonding (O2W–H2WA···O3, O2W–H2WB···O1W).

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.199 × 0.253 × 0.327 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.27 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3778, 2214
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1552
$N(param)_{refined}$:	172
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

* Correspondence author (e-mail: guangbochejl@yahoo.com)

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.5393	0.2230	0.4962	0.040
H(6)	2*i*	0.8599	0.4893	0.3669	0.052
H(7)	2*i*	0.7992	0.6344	0.1951	0.049
H(9)	2*i*	1.2547	0.2424	–0.0415	0.059
H(10)	2*i*	1.3068	0.1074	0.1355	0.062
H(4)	2*i*	0.9481	–0.0638	0.1891	0.044
H(3)	2*i*	1.1051	0.2342	0.3294	0.050
H(1)	2*i*	0.2031	0.6066	0.3857	0.075
H(1WA)	2*i*	1.2568	–0.2138	–0.0228	0.102
H(1WB)	2*i*	1.2681	–0.3099	0.0901	0.102
H(2WA)	2*i*	0.3750	0.9261	0.3147	0.093
H(2WB)	2*i*	0.3790	0.8170	0.2230	0.180

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.5929(2)	0.2554(2)	0.3008(1)	0.0332(8)	0.0301(7)	0.0303(9)	–0.0059(7)	–0.0111(6)	0.0076(6)
C(2)	2*i*	0.6175(2)	0.1802(2)	0.4112(1)	0.0323(8)	0.0314(7)	0.0262(8)	–0.0017(6)	–0.0084(6)	0.0061(6)
C(3)	2*i*	0.7822(2)	0.0291(2)	0.3678(1)	0.0328(7)	0.0291(7)	0.0260(8)	–0.0052(7)	–0.0101(6)	0.0057(6)
C(4)	2*i*	0.4421(2)	0.4206(2)	0.2869(2)	0.0347(8)	0.0328(8)	0.0336(9)	–0.0044(7)	–0.0124(7)	0.0079(7)
C(5)	2*i*	0.8893(2)	–0.1111(2)	0.4348(2)	0.0350(8)	0.0278(7)	0.033(1)	–0.0052(7)	–0.0138(7)	0.0069(7)
C(6)	2*i*	0.9389(3)	0.4402(2)	0.2834(2)	0.0475(9)	0.0459(9)	0.0308(9)	–0.0124(8)	–0.0106(7)	0.0085(7)
C(7)	2*i*	0.9024(3)	0.5270(2)	0.1809(2)	0.0456(9)	0.0384(8)	0.0306(9)	–0.0074(8)	–0.0118(7)	0.0073(7)
C(8)	2*i*	1.0193(2)	0.4547(2)	0.0565(1)	0.0341(8)	0.0353(8)	0.0298(9)	–0.0111(7)	–0.0113(7)	0.0094(7)
C(9)	2*i*	1.1726(3)	0.2948(2)	0.0407(2)	0.051(1)	0.0453(9)	0.0297(9)	0.0031(8)	–0.0104(8)	0.0078(7)
C(10)	2*i*	1.2030(3)	0.2142(2)	0.1464(2)	0.051(1)	0.0451(9)	0.043(1)	–0.0007(8)	–0.0167(8)	0.0132(8)
N(1)	2*i*	0.8463(2)	0.0204(1)	0.2380(1)	0.0382(7)	0.0287(6)	0.0288(7)	0.0034(5)	–0.0108(6)	0.0038(5)
N(2)	2*i*	0.7342(2)	0.1571(2)	0.1942(1)	0.0390(7)	0.0323(6)	0.0302(7)	–0.0008(6)	–0.0124(6)	0.0074(5)
N(3)	2*i*	1.0855(2)	0.2873(2)	0.2641(1)	0.0460(8)	0.0469(7)	0.0320(8)	–0.0151(7)	–0.0178(6)	0.0183(6)
O(1)	2*i*	0.3067(2)	0.4999(1)	0.3979(1)	0.0550(7)	0.0358(6)	0.0331(7)	0.0108(5)	–0.0116(6)	0.0055(5)
O(2)	2*i*	0.4448(2)	0.4752(1)	0.1833(1)	0.0526(7)	0.0447(6)	0.0354(7)	0.0037(6)	–0.0142(5)	0.0151(5)
O(1W)	2*i*	1.2139(2)	–0.2219(2)	0.0713(1)	0.0766(9)	0.0545(7)	0.0359(7)	0.0113(7)	–0.0105(6)	0.0016(6)
O(3)	2*i*	0.8223(2)	–0.0972(1)	0.5546(1)	0.0475(6)	0.0410(6)	0.0303(7)	–0.0014(5)	–0.0108(5)	0.0126(5)
O(2W)	2*i*	0.4619(2)	0.8523(2)	0.2475(1)	0.0551(8)	0.0573(8)	0.0581(9)	–0.0042(7)	–0.0049(7)	–0.0084(7)
O(4)	2*i*	1.0389(2)	–0.2323(1)	0.3633(1)	0.0645(8)	0.0363(6)	0.0404(7)	0.0152(6)	–0.0178(6)	0.0008(5)

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