

Crystal structure of 4-(4-pyridyl)-3,5-dimethylpyrozole hydrate, $(C_5H_4N)CH_3(C_3N_2H)CH_3 \cdot H_2O$

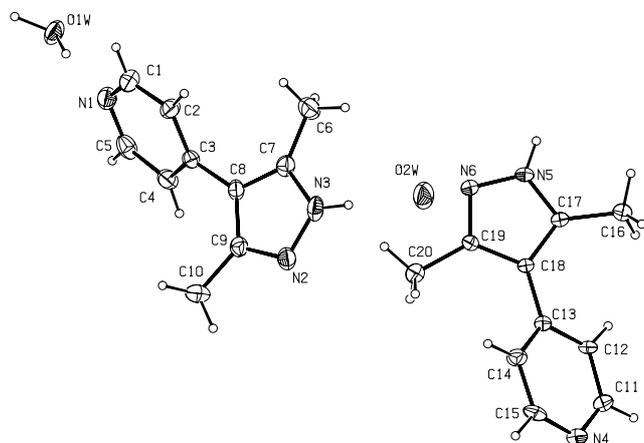
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Abstract

$C_{10}H_{13}N_3O$, triclinic, $P\bar{1}$ (no. 2), $a = 7.475(2)$ Å, $b = 9.171(2)$ Å, $c = 15.536(3)$ Å, $\alpha = 80.88(3)^\circ$, $\beta = 89.91(3)^\circ$, $\gamma = 81.24(3)^\circ$, $V = 1039.0$ Å³, $Z = 4$, $R_{gt}(F) = 0.063$, $wR_{ref}(F^2) = 0.085$, $T = 293$ K.

Source of material

A solution of 3.54 g (0.02 mol) 3-(4-pyridyl)pentane-2,4-dione and 2.14 g (0.02 mol) hydrazine hydrate solution (30 % a.q.) in 30 ml methanol was refluxed for half of an hour. The solvent was removed and the residual was washed with water. The product was recrystallized in acetone. The yellow crystals were obtained by evaporating the solution at the room temperature.

Experimental details

The H atoms of one water molecule (O1W) were located by difference Fourier maps and were refined isotropically. The H atoms of the other water molecule (O2W) were not found. The positions of other hydrogen atoms were calculated.

Discussion

An increasing interest has been paid attention to self-assembling polymetallic coordination compounds and supermolecules which usually possess interesting structures and potential application such as inclusion and shape-selective catalysis [1-4]. Here we describe the crystal structure of the new ligand 4-(4-pyridyl)-3,5-dimethylpyrozole (I) and compare its structure and coordination properties with other similar compound.

The structure consists of two independent molecules, which have the same composition but slightly different structures. In the two molecules, the lengths of N—C of pyridyl (py) and C—N and N—N of 3,5-dimethylpyrozole (dipz) are slightly different. The bond angles $\angle N-N-C$ are somewhat different, in one molecule (figure, left) they are $105.6(2)^\circ$ and $111.3(2)^\circ$ while in the other molecule (figure, right) they are $103.8(2)^\circ$ and $113.8(2)^\circ$.

In I, the bond lengths C—N ($1.319(4)$ Å – $1.355(3)$ Å) and N—N ($1.336(2)$ Å – $1.370(3)$ Å) of dipz ring agree well with those in similar compounds such as 3,5-dimethylpyrazole in $[C_{10}H_{10}NO_2]_2 \cdot 2H_2O$ (II) [2]. The C—N bond lengths are in the range $1.319(4)$ Å to $1.342(4)$ Å. The bond angles $\angle N-C-C$ ($106.0(2)^\circ$ – $112.4(2)^\circ$) of pz in I are similar to those angles in II, while the bond angles $\angle C-N-N$ ($103.8(2)^\circ$ – $113.8(2)^\circ$) of pz in I are shorter than those in II. The bond angles $\angle N-C-C$ are from $124.0(3)^\circ$ to $126.4(3)^\circ$. Since the ligand I has two coordinating moieties, py and dipz, it has more diverse coordination modes than similar compounds (II), namely two monodentate modes, two bidentate modes and one tridentate mode.

Table 1. Data collection and handling.

Crystal:	yellow block, size $0.12 \times 0.47 \times 0.54$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	0.83 cm^{-1}
Diffractometer, scan mode:	Rigaku R-axis RAPID IP, ω/φ
$2\theta_{\text{max}}$:	54.98°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	6798, 4535
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1570
$N(\text{param})_{\text{refined}}$:	254
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(3A)	2i	-0.3698	0.1650	0.5022	0.079
H(5A)	2i	0.2601	0.1823	0.9873	0.056
H(1B)	2i	0.0997	0.6676	0.2513	0.085
H(2B)	2i	-0.1040	0.5246	0.3086	0.068
H(4B)	2i	0.3074	0.1916	0.3800	0.071
H(5B)	2i	0.4973	0.3516	0.3221	0.080
H(6B)	2i	-0.3549	0.4159	0.5178	0.117
H(6C)	2i	-0.2804	0.5093	0.4360	0.117
H(6D)	2i	-0.1532	0.4440	0.5176	0.117
H(10A)	2i	0.0002	-0.1015	0.3410	0.112
H(10B)	2i	0.1680	-0.0207	0.3500	0.112
H(10C)	2i	0.0319	0.0344	0.2708	0.112

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(11A)	2i	0.3108	-0.5862	1.1151	0.063
H(12A)	2i	0.3393	-0.3381	1.0952	0.051
H(14A)	2i	0.1734	-0.3059	0.8474	0.062
H(15A)	2i	0.1638	-0.5568	0.8753	0.068
H(16A)	2i	0.1649	0.0528	1.1185	0.076
H(16B)	2i	0.2604	-0.1138	1.1384	0.076
H(16C)	2i	0.0602	-0.0764	1.1022	0.076
H(20A)	2i	0.4383	-0.0165	0.7543	0.094
H(20B)	2i	0.3237	-0.1476	0.7698	0.094
H(20C)	2i	0.5213	-0.1710	0.8086	0.094
H(1W)	2i	0.631(4)	0.767(3)	0.215(1)	0.091
H(2W)	2i	0.485(3)	0.653(3)	0.260(2)	0.091

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(1)	2i	0.3222(4)	0.5263(3)	0.2814(2)	0.077(2)	0.071(2)	0.055(2)	-0.028(2)	0.014(2)	-0.012(2)
N(2)	2i	-0.2030(3)	0.0499(3)	0.4288(2)	0.071(2)	0.072(2)	0.048(2)	-0.025(2)	0.013(2)	-0.016(2)
N(3)	2i	-0.2797(3)	0.1675(3)	0.4678(2)	0.067(2)	0.087(2)	0.048(2)	-0.032(2)	0.019(2)	-0.008(2)
N(4)	2i	0.2347(3)	-0.5988(3)	0.9970(2)	0.062(2)	0.036(2)	0.061(2)	-0.008(1)	0.003(2)	-0.009(2)
N(5)	2i	0.2764(3)	0.1010(2)	0.9654(2)	0.064(2)	0.029(2)	0.050(2)	-0.012(1)	0.008(1)	-0.014(1)
N(6)	2i	0.3367(3)	0.0939(2)	0.8849(2)	0.065(2)	0.032(2)	0.046(2)	-0.010(1)	0.010(1)	-0.006(1)
C(1)	2i	0.1425(5)	0.5708(4)	0.2785(2)	0.089(3)	0.064(3)	0.059(2)	-0.022(3)	0.012(2)	-0.001(2)
C(2)	2i	0.0185(4)	0.4852(3)	0.3123(2)	0.057(2)	0.048(2)	0.060(2)	-0.006(2)	0.006(2)	0.002(2)
C(3)	2i	0.0741(4)	0.3399(3)	0.3521(2)	0.050(2)	0.045(2)	0.036(2)	-0.008(2)	-0.001(2)	-0.011(2)
C(4)	2i	0.2609(4)	0.2888(3)	0.3549(2)	0.059(2)	0.058(2)	0.063(2)	-0.006(2)	0.010(2)	-0.021(2)
C(5)	2i	0.3737(4)	0.3869(5)	0.3192(2)	0.049(2)	0.093(3)	0.069(3)	-0.024(3)	0.015(2)	-0.039(2)
C(6)	2i	-0.2508(4)	0.4264(3)	0.4824(2)	0.088(3)	0.074(3)	0.084(3)	-0.030(2)	0.030(2)	-0.036(2)
C(7)	2i	-0.1954(4)	0.2881(3)	0.4453(2)	0.057(2)	0.062(2)	0.046(2)	-0.025(2)	0.003(2)	-0.011(2)
C(8)	2i	-0.0550(4)	0.2444(3)	0.3916(2)	0.062(2)	0.062(2)	0.040(2)	-0.027(2)	0.014(2)	-0.015(2)
C(9)	2i	-0.0668(4)	0.0978(3)	0.3832(2)	0.057(2)	0.054(2)	0.038(2)	-0.010(2)	0.000(2)	-0.004(2)
C(10)	2i	0.0432(4)	-0.0069(3)	0.3316(2)	0.094(3)	0.047(2)	0.084(3)	-0.006(2)	0.005(2)	-0.020(2)
C(11)	2i	0.2854(4)	-0.5301(3)	1.0600(2)	0.063(2)	0.036(2)	0.053(2)	-0.001(2)	0.003(2)	0.003(2)
C(12)	2i	0.3027(4)	-0.3796(3)	1.0485(2)	0.054(2)	0.023(2)	0.052(2)	-0.005(2)	0.005(2)	-0.010(2)
C(13)	2i	0.2654(4)	-0.2906(3)	0.9671(2)	0.049(2)	0.033(2)	0.041(2)	-0.010(2)	0.006(2)	-0.009(2)
C(14)	2i	0.2067(4)	-0.3598(3)	0.9024(2)	0.066(2)	0.042(2)	0.050(2)	-0.016(2)	-0.002(2)	-0.011(2)
C(15)	2i	0.1983(4)	-0.5118(3)	0.9209(2)	0.066(2)	0.042(2)	0.070(3)	-0.010(2)	-0.001(2)	-0.032(2)
C(16)	2i	0.1762(3)	-0.0433(3)	1.1002(2)	0.054(2)	0.042(2)	0.053(2)	-0.000(2)	0.006(2)	-0.007(2)
C(17)	2i	0.2432(3)	-0.0318(3)	1.0091(2)	0.040(2)	0.027(2)	0.042(2)	-0.004(1)	-0.001(2)	-0.004(2)
C(18)	2i	0.2839(3)	-0.1334(3)	0.9529(2)	0.043(2)	0.026(2)	0.037(2)	-0.005(2)	0.004(2)	-0.005(2)
C(19)	2i	0.3404(4)	-0.0483(3)	0.8770(2)	0.049(2)	0.034(2)	0.039(2)	-0.001(2)	0.006(2)	-0.008(2)
C(20)	2i	0.4124(4)	-0.1006(3)	0.7950(2)	0.088(3)	0.049(2)	0.048(2)	-0.008(2)	0.009(2)	-0.002(2)
O(1W)	2i	0.5957(3)	0.7063(2)	0.2708(1)	0.101(2)	0.075(2)	0.061(2)	-0.049(2)	0.016(2)	-0.003(1)
O(2W)	2i	-0.5753(3)	0.1609(2)	0.5812(1)	0.144(2)	0.107(2)	0.085(2)	-0.077(2)	0.051(2)	-0.037(2)

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