Crystal structure of ammonium 5-carboxypicolinate monohydrate, $C_7H_{10}N_2O_5$

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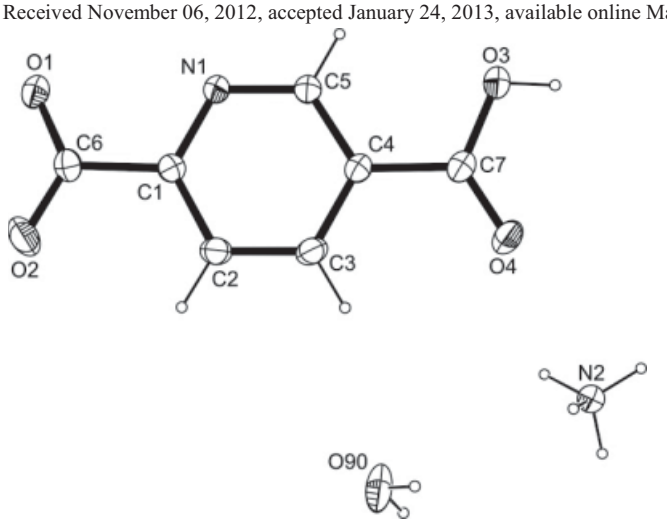

Abstract

$C_7H_{10}N_2O_5$, triclinic, $P1$ (no. 1), a = 3.7899(2) Å, b = 6.1661(3) Å, c = 9.3089(4) Å, α = 91.876(2)°, β = 92.926(2)°, γ = 90.872(2)°, V = 217.1 Å^3, Z = 1, $R_{gt}(F)$ = 0.0298, $wR_{ref}(F^2)$ = 0.0784, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless rods, size 0.208×0.276×0.546 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.33 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	55.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3316, 100
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 994
$N(param)_{refined}$:	152
Programs:	SHELX [2], ORTEP-3 [3], MERCURY [4], PLATON [5]

Source of material

Pyridine-2,5-dicarboxylic acid was suspended in aqueous ammonium hydroxide and the mixture was heated until complete dissolution of the solid. Upon cooling to room temperature and free evaporation of the solvent, crystals suitable for the X-ray diffraction study were obtained.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H = 0.95 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atom of the hydroxyl group was allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [2]), with U_{iso}(H) set to 1.5U_{eq}(O). All nitrogen-bound H atoms as well as the H atoms of the water molecule were located on a difference Fourier map and refined freely. Friedel opposites (806 pairs) have been merged.

Discussion

The synthesis of metal-organic framework (MOF) structures is a current topic of research in coordination chemistry. Among the key steps to be understood are the rules guiding the formation of these MOFs to allow for the tailored synthesis of structures with defined pore sizes. Polyfunctional and polydentate ligands such as aromatic carboxylic acids have attracted much attention in this aspect [1] as the variation of substitution patterns on the aromatic core allows for the fine-tuning of spatial, electronic and chemical properties of the envisioned porous structures on a broad basis. At the beginning of a comprehensive study about carboxylate-based coordination compounds, the structure of the title compound was determined to gather information about metrical parameters of the non-coordinated ligand to allow for comparisons with respective values found in coordination compounds to be synthesized. The title compound is the monoammonium salt of pyridine-2,5-dicarboxylic acid. The compound crystallizes in the non-centrosymmetric space group $P1$ with one ammonium cation, one aromatic anion and one additional molecule of water in the asymmetric unit. The aromatic anion is essentially flat (r.m.s. of all fitted hydrogen and non-hydrogen atoms = 0.0935 Å). The least-squares planes defined by the non-hydrogen atoms of the pyridine moiety on the one hand and the individual atoms of the carboxylic acid groups on the other hand enclose angles of 7.7(2)° and 8.3(2)° with the smaller angle realized by the protonated carboxylic acid group. The crystal structure of the title compound is dominated by hydrogen bonds. These are supported by all hydrogen atoms bound to nitrogen and oxygen atoms as donors and nearly all possible hetero atoms as acceptors, the only non-participating one being the oxygen atom of the still protonated hydroxy group. In total, the entities of the title structure are connected by eight different hydrogen bonds to a three-dimensional network. The shortest intercentroid distance between two aromatic systems was found at 3.7899(8) Å which is in agreement with the length of the unit cell axis a.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	1*a*	–0.3157	1.1938	0.5181	0.039
H(2)	1*a*	0.3241	0.3474	0.2556	0.025
H(3A)	1*a*	0.2223	0.5698	0.4591	0.025
H(5)	1*a*	–0.1957	1.0153	0.1927	0.023
H(901)	1*a*	0.450(7)	0.382(4)	0.708(3)	0.032(6)
H(902)	1*a*	0.765(8)	0.411(5)	0.709(3)	0.040(7)
H(21)	1*a*	0.699(6)	0.921(4)	0.757(3)	0.031(6)
H(22)	1*a*	0.746(8)	0.858(5)	0.908(3)	0.044(7)
H(23)	1*a*	0.434(8)	0.790(5)	0.830(3)	0.038(6)
H(24)	1*a*	0.476(8)	1.016(5)	0.877(3)	0.042(7)

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}
O(1)	1*a*	0.1324(3)	0.5112(2)	–0.1455(1)	0.0256(5)	0.0249(5)	0.0174(5)	0.0001(4)	0.0012(4)	–0.0023(4)
O(2)	1*a*	0.2862(5)	0.2342(2)	–0.0062(2)	0.070(1)	0.0223(6)	0.0298(7)	0.0160(6)	0.0118(6)	–0.0004(5)
O(3)	1*a*	–0.2677(3)	1.1266(2)	0.4419(1)	0.0366(6)	0.0242(5)	0.0177(5)	0.0084(4)	0.0005(4)	–0.0033(4)
O(4)	1*a*	0.0213(3)	0.9095(2)	0.5953(1)	0.0339(6)	0.0417(7)	0.0146(5)	0.0102(5)	0.0000(4)	–0.0002(4)
N(1)	1*a*	–0.0260(3)	0.7541(2)	0.0896(1)	0.0237(6)	0.0180(5)	0.0148(5)	0.0032(5)	0.0007(4)	0.0000(4)
C(1)	1*a*	0.1228(3)	0.5603(2)	0.1093(1)	0.0163(6)	0.0173(6)	0.0172(6)	0.0004(4)	0.0018(4)	0.0005(5)
C(2)	1*a*	0.2189(4)	0.4853(2)	0.2454(2)	0.0215(7)	0.0200(6)	0.0209(7)	0.0036(5)	0.0009(5)	0.0042(5)
C(3)	1*a*	0.1577(4)	0.6159(2)	0.3651(2)	0.0230(7)	0.0233(7)	0.0165(6)	0.0020(5)	–0.0013(5)	0.0036(5)
C(4)	1*a*	–0.0001(3)	0.8159(2)	0.3454(1)	0.0177(6)	0.0198(6)	0.0148(6)	–0.0002(5)	0.0012(4)	0.0004(5)
C(5)	1*a*	–0.0878(3)	0.8788(2)	0.2059(1)	0.0228(7)	0.0178(6)	0.0164(6)	0.0029(5)	0.0010(5)	0.0006(5)
C(6)	1*a*	0.1858(4)	0.4221(2)	–0.0250(2)	0.0218(7)	0.0196(6)	0.0194(6)	0.0001(5)	0.0043(5)	–0.0017(5)
C(7)	1*a*	–0.0787(3)	0.9551(2)	0.4736(1)	0.0181(6)	0.0239(7)	0.0158(6)	–0.0014(5)	0.0011(5)	–0.0002(5)
O(90)	1*a*	0.6123(3)	0.3715(2)	0.6607(1)	0.0253(6)	0.0475(7)	0.0241(6)	0.0020(5)	0.0013(5)	–0.0171(5)
N(2)	1*a*	0.5781(3)	0.8980(2)	0.8416(1)	0.0248(6)	0.0208(6)	0.0174(5)	0.0043(4)	0.0001(4)	0.0001(4)

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