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Redetermination of the crystal structure of ammonium formiate at 200 K, CH_5NO_2

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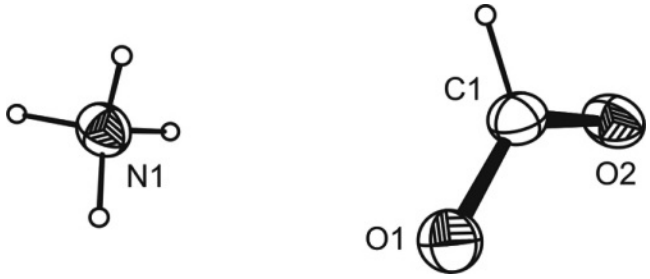
Received October 18, 2013, accepted March 31, 2014, available online April 10, 2014, CCDC no. 1267/4090



Abstract

CH_5NO_2, monoclinic, *Pc* (no. 7), a = 3.7747(3) Å, b = 4.6743(3) Å, c = 9.0947(8) Å, β = 90.642(4)°, V = 160.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.0168, $wR_{ref}(F^2)$ = 0.0427, T = 200(2) K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.47×0.28×0.19 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.24 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2516, 386
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 386
$N(param)_{refined}$:	58
Programs:	SHELX [5], ORTEP-3 [6], MERCURY [7], PLATON [8]

Source of material

The compound was obtained commercially (Merck). Crystals suitable for the X-ray structure analysis were taken directly from the provided product.

Experimental details

Due to the absence of a strong anomalous scatterer, the Flack parameter is meaningless. Thus, Friedel opposites (377 pairs) have been merged and the item was removed from the CIF. All H atoms were located on a difference Fourier map and refined freely.

Discussion

The synthesis of metal-organic framework (MOF) structures has been a topic of considerable research activity over the past years. Owing to the many envisioned applications of MOFs in catalytic processes, a rationalization of their synthesis procedures to allow for the tailored synthesis of various pore sizes seemed desireable. A modular approach based on individual secondary building blocks was suggested in this aspect that was specifically based on (multibasic) carboxylic acids [1]. In continuation of our ongoing research in the structural diversity and bonding patterns that can be accomplished by simple mono- and bidentate ligands, a project about formic acid as the simplest carboxylic acid as a bonding partner was initiated. To allow for the comparison of the influence of hydrogen bonding on structural parameters, the ammonium salt of this acid was chosen as a starting point. Although the structure of the latter compound has been determined earlier, data is only available at room temperature [2]. As molecular and crystal structures of target molecules are to be determined at low temperature, the structure of the title compound was re-determined to enable comparisons of individual metrical parameters throughout the whole series. The formiate anion is planar. C–O bond lengths of 1.2496(12) and 1.2502(13) Å, respectively, are nearly identical due to resonance stabilization of the carboxylate. These values are, therefore, found to be slightly longer than the corresponding bond lengths at room temperature for this compound that were reported to be around 1.23-1.24 Å [2]. All of the nitrogen-bound hydrogen atoms participate in hydrogen bonds with both oxygen atoms of the formiate anion acting as acceptors. A graph-set analysis showed, that besides some trivial discrete- and chain-type hydrogen bonding motifs a third level ring motif ($R_6^5(16)$) is characteristic for this structure [3, 4]. In total, the entities of the compound are connected to a three-dimensional network in the crystal structure.

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*a*	−1.075(5)	−0.545(4)	−0.437(2)	0.035(4)
H(1B)	2*a*	−0.795(5)	−0.439(4)	−0.515(2)	0.032(3)
H(1)	2*a*	−0.442(4)	−1.024(4)	−0.747(2)	0.035(4)
H(1C)	2*a*	−0.810(4)	−0.733(3)	−0.487(2)	0.030(3)
H(1D)	2*a*	−1.046(5)	−0.601(3)	−0.587(2)	0.033(4)

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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)	2*a*	–0.3250(2)	–0.6379(1)	–0.76754(8)	0.0344(4)	0.0275(4)	0.0219(3)	–0.0040(3)	–0.0039(2)	–0.0010(3)
O(2)	2*a*	–0.5254(2)	–0.9283(2)	–0.94376(8)	0.0339(4)	0.0222(3)	0.0269(4)	–0.0019(3)	–0.0049(3)	–0.0019(3)
C(1)	2*a*	–0.4286(2)	–0.8750(2)	–0.8146(1)	0.0293(4)	0.0220(4)	0.0228(4)	–0.0004(3)	–0.0005(3)	0.0037(3)
N(1)	2*a*	–0.9262(2)	–0.5807(2)	–0.50709(9)	0.0243(4)	0.0212(4)	0.0222(4)	0.0009(3)	–0.0033(3)	–0.0014(3)

Acknowledgments. The authors thank Mr Derek Buss for helpful discussions.

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