

1*H*-Benzimidazole-2-carboxylic acid monohydrateSławomir Krawczyk,^a Maria Gdaniec^{a*} and Franciszek Sączewski^b^aFaculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland, and
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Key indicators

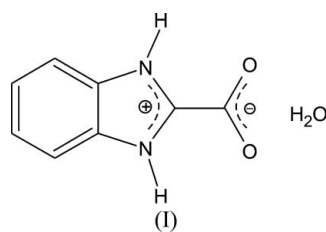
Single-crystal X-ray study
T = 130 K
Mean $\sigma(\text{C}-\text{C})$ = 0.005 Å
R factor = 0.053
wR factor = 0.096
Data-to-parameter ratio = 11.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1*H*-Benzimidazole-2-carboxylic acid crystallizes as the monohydrate, C₈H₆N₂O₂·H₂O, and the organic molecule exists in a zwitterionic form, *viz.* 1*H*-benzimidazolium-2-carboxylate. Hydrogen bonds connect the molecules of acid and water into a two-dimensional network.

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Comment

1*H*-Benzimidazole-2-carboxylic acid, a simple carboxylic acid synthesized for the first time by Bistrzycki & Przeworski (1912), has not found any important application until now. Recently, it has been noticed that, in its doubly deprotonated form, it might be a good bridging ligand in the formation of polymeric transition metal complexes (Rettig *et al.*, 1999). Nevertheless, reports on its use in coordination chemistry are very scarce (Carballo *et al.*, 1996; Patch *et al.*, 1987; Rettig *et al.*, 1999). The compound attracted our attention when, in the reaction of 2-(oxazolin-2-yl)benzimidazole with CuCl₂ in DMF (Sączewski *et al.*, 2005), the Cu^{II} complex with the 1*H*-benzimidazole-2-carboxylate ligand, bis[(μ_2 -chloro)-(1*H*-benzimidazole-2-carboxylato)dimethylformamide-copper(II)], was unexpectedly obtained. It was evident from its crystal structure that, as a monoanion, the acid can form transition metal complexes that are assembled *via* N—H···O hydrogen bonds into polymeric tapes and that these complexes might be analogues of polymeric coordination compounds formed by the dianion (Fig. 1).



To obtain more information, mainly about the tautomeric form and assembly mode of 1*H*-benzimidazole-2-carboxylic acid, we determined the crystal structure of its monohydrate, (I). The asymmetric unit of (I) is shown in Fig. 2. As both N atoms of the benzimidazole group are protonated, it exists in the zwitterionic form. This is additionally confirmed by equal bond lengths N1—C2 and C2—N3 of the imidazolium fragment, and C10—O1 and C10—O2 of the carboxylate group (Table 1). The molecule is approximately planar, with a dihedral angle between the benzimidazole and carboxylate groups of 5.0 (2)°. Hydrogen bonds connect the constituent molecules into a two-dimensional network (Fig. 3). The geometry of the hydrogen bonds is given in Table 2. The aminocarboxylate function generates, on one side, a centro-

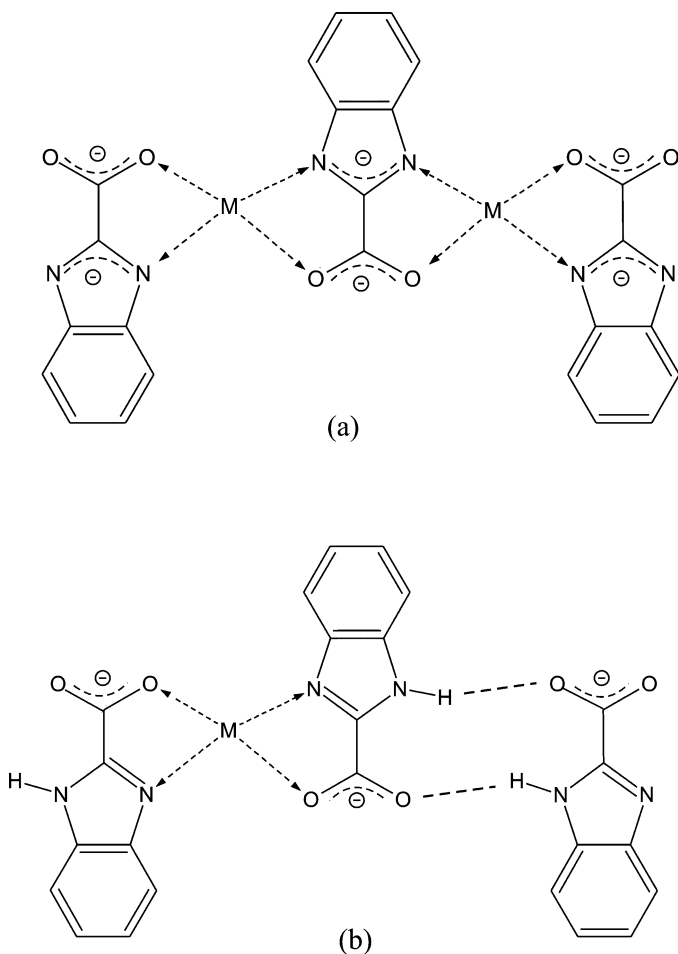


Figure 1
 (a) Possible polymeric coordination compounds formed by the dianion.
 (b) Hydrogen-bonded tapes formed by coordination compounds of the monoanion. (*M* = transition metal).

symmetric hydrogen-bond motif $R_2^2(10)$, whereas on the opposite side, owing to the mediating role played by water molecules, an $R_4^4(14)$ centrosymmetric motif is formed. The polymeric tapes thus formed are further assembled into a two-dimensional network *via* O—H...O hydrogen bonds between water molecules and carboxylate groups.

Experimental

The title compound was prepared by the method of Bistrzycki & Przeworski (1912). Small needle-shaped single crystals were obtained by recrystallization of (I) from ethanol.

Crystal data

$C_8H_6N_2O_2 \cdot H_2O$	$Z = 2$
$M_r = 180.16$	$D_x = 1.494 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 4.4080 (15) \text{ \AA}$	Cell parameters from 2151 reflections
$b = 8.877 (3) \text{ \AA}$	$\theta = 4-25^\circ$
$c = 10.757 (3) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\alpha = 72.20 (3)^\circ$	$T = 130 (2) \text{ K}$
$\beta = 87.67 (3)^\circ$	Needle, colourless
$\gamma = 88.53 (3)^\circ$	$0.5 \times 0.07 \times 0.01 \text{ mm}$
$V = 400.4 (2) \text{ \AA}^3$	

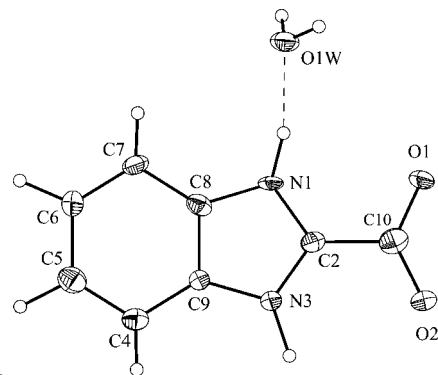


Figure 2
 The molecular structure of (I), with 50% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

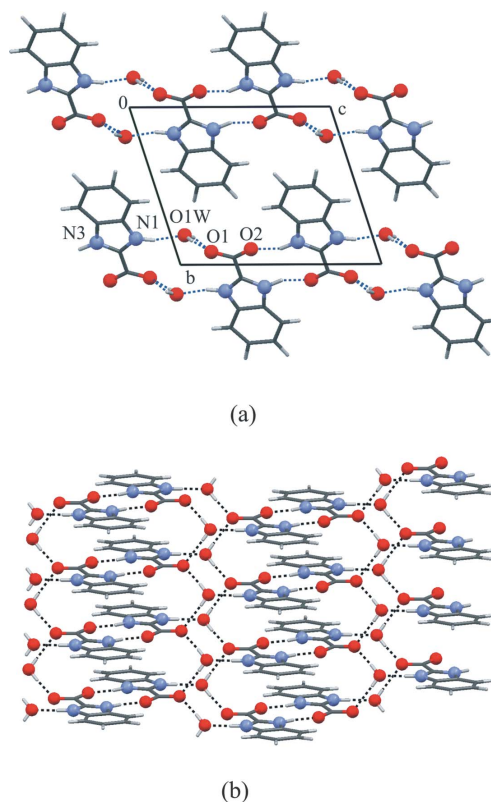


Figure 3
 The crystal structure of (I). (a) The crystal packing viewed along the *a* axis. (b) The two-dimensional network of hydrogen-bonded (dashed lines) molecules.

Data collection

Kuma KM-4 CCD κ geometry diffractometer	724 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.080$
Absorption correction: none	$\theta_{\text{max}} = 25.0^\circ$
3051 measured reflections	$h = -5 \rightarrow 2$
1407 independent reflections	$k = -10 \rightarrow 10$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0154P)^2]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1407 reflections	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
119 parameters	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

O1—C10	1.254 (4)	C2—N3	1.335 (4)
O2—C10	1.247 (4)	C2—C10	1.501 (4)
N1—C2	1.341 (4)	N3—C9	1.384 (4)
N1—C8	1.386 (4)		
C2—N1—C8	108.6 (3)	O2—C10—O1	128.9 (3)
N3—C2—N1	108.9 (3)	O2—C10—C2	116.2 (3)
C2—N3—C9	109.5 (3)	O1—C10—C2	114.8 (3)
O1—C10—C2—N1	−4.2 (5)	O2—C10—C2—N3	−3.0 (5)

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 ^W	0.90	1.76	2.646 (3)	166
N3—H3...O2 ^I	0.90	1.82	2.686 (3)	160
O1 ^W —H2 ^W ...O1 ^{II}	0.85	1.93	2.764 (3)	165
O1 ^W —H1 ^W ...O1 ^{III}	0.85	1.93	2.782 (3)	176

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 1, -y, -z$; (iii) $-x, -y, -z$.

All H atoms were located in electron-density difference maps. H atoms bonded to C atoms were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (C—H = 0.93–1.09 Å). O—H and N—H were set to 0.85

and 0.90 Å, respectively, and these H atoms were refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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