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Benzimidazolium hydrogen bis(3-carboxyphenoxyacetate)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.069
wR factor = 0.196
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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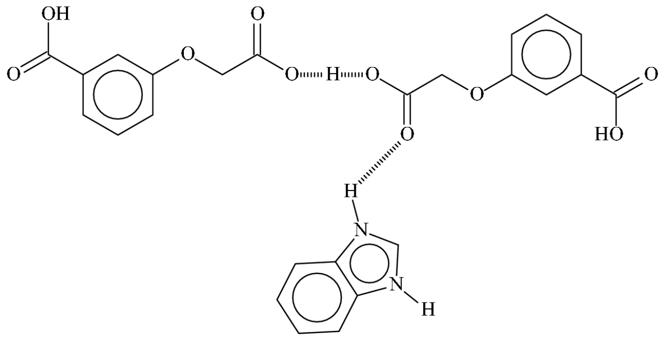
The anion in the structure of the title compound, $C_7H_7N_2^+ \cdot H^+ \cdot 2C_9H_7O_5^-$, has a CO_2H unit on the aromatic ring. Two anions are linked through an 'acid H' atom (which lies on a center of inversion) to give a monoanionic entity. Adjacent entities are linked into a linear chain through hydrogen bonding involving the CO_2H units. The chains are connected into a layer structure through the benzimidazolium cations, which possess C_2 symmetry.

Comment

The reaction of nickel(II) acetate with 3-carboxyphenoxyacetic acid furnishes tetraaquabis(carboxyphenoxyacetate)nickel(II); the metal atom is coordinated by the carboxyl CO_2 unit of the oxyacetate arm (Gao *et al.*, 2004). As the CO_2H substituent of the ring has an acidic H atom, the present investigation was initiated to ascertain if it could be neutralized by benzimidazole, as in the analogous cadmium complex. However, the reaction yielded instead the title compound, which is an organic salt, (I).



(I)

Carboxylic acids generally afford ammonium carboxylates when reacted with monoamines, but some react with only half an equivalent of the amine to yield an ammonium carboxylate–carboxylic acid complex, *e.g.* 3-hydroxypyridinium hydrogen bis(4-nitrobenzoate) (Lynch *et al.*, 1999), piperidinium hydrogen bis(4-bromobenzoate) (Misaki *et al.*, 1989*a*), pyrrolidinium hydrogen bis(4-methylbenzoate) (Misaki *et al.*, 1989*b*) and tetramethylammonium hydrogen bis[bis(dimethyldithiocarbamyl)acetate] (Ng, 1997). In these salt/acid compounds, an 'acid H' atom is present, located midway between the negatively charged carboxyl O atoms of the two carboxylate entities; in fact, a central feature is their close proximity of *ca* 2.5 Å.

The benzimidazolium derivative of 3-carboxyphenoxyacetic acid also displays this feature, which involves the oxyacetate substituent of the aromatic ring, as shown in Fig. 1. Selected

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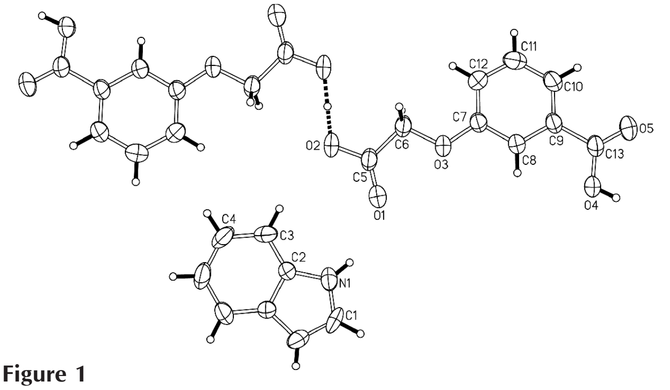

Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. Dashed lines indicate a symmetrical hydrogen bond.

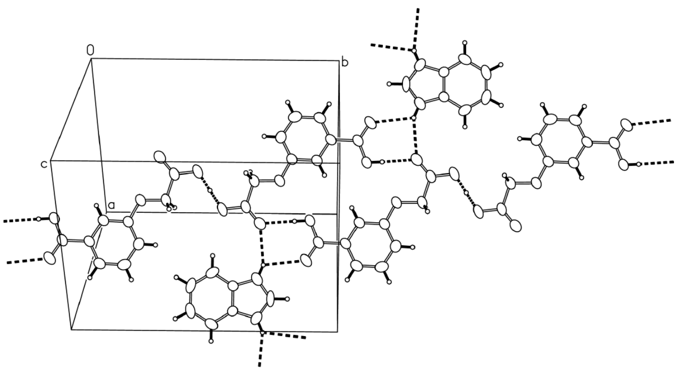

Figure 2
*ORTEP*II (Johnson, 1976) plot of the layer structure of (I), with displacement ellipsoids at the 50% probability level. Dashed lines indicate hydrogen bonds.

bond distances and angles are given in Table 1. As the acidic H atom in the carboxyl CO_2H substituent is retained, it engages in hydrogen-bonding interactions to form a chain. The chains are connected by N—H···O hydrogen bonds into a layer structure through the 3-carboxyphenoxyacetate cations (Fig. 2); details of the hydrogen bonding are given in Table 2.

The parent acid crystallizes as a monohydrate and the acid is linked to another molecule to form a dimer. The dimers are then linked *via* hydrogen bonds to the water molecules to form a three-dimensional network (Gu *et al.*, 2004).

The benzimidazolium cation, which possesses C_2 symmetry in this structure, is not commonly used as a counter-ion, as revealed by a cursory search of the Cambridge Structural Database (Version 5.25; Allen, 2002). Only two examples were found, which were 3- and 4-nitrobenzoate derivatives (Hashizume *et al.*, 2001).

Experimental

Cadmium dinitrate tetrahydrate (3.08 g, 10 mmol), benzimidazole (1.18 g, 10 mmol) and 3-carboxyphenoxyacetic acid (1.96 g, 10 mmol) were dissolved in a small volume of a 1:1 ethanol–water mixture. The solution was sealed in a 25 ml Teflon-lined stainless steel bomb, which was heated at 423 K for 120 h. Colorless crystals were separated from the filtered solution after several days. Analysis calculated for $C_{25}H_{22}N_2O_{10}$: C 58.82, H 4.34, N 5.49%; found: C 58.99, H 4.27, N 5.28%.

Crystal data

$C_7H_7N_2^+\cdot H^+\cdot 2C_9H_7O_5^-$
$M_r = 510.45$
Monoclinic, $C2/c$
$a = 11.255$ (2) Å
$b = 14.108$ (3) Å
$c = 14.576$ (3) Å
$\beta = 103.37$ (3)°
$V = 2251.9$ (8) Å^3
$Z = 4$

$D_x = 1.506$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7992 reflections
$\theta = 3.2$–27.4°
$\mu = 0.12$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.40 × 0.28 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.844$, $T_{\max} = 0.977$
10 631 measured reflections

2575 independent reflections
2105 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -18 \rightarrow 18$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.196$
$S = 1.18$
2575 reflections
177 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2 + 3.922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.222 (4)	C3—C4	1.378 (5)
O2—C5	1.291 (3)	C4—C4^{i}	1.393 (8)
O3—C7	1.367 (3)	C5—C6	1.512 (4)
O3—C6	1.414 (3)	C7—C8	1.389 (4)
O4—C13	1.305 (4)	C7—C12	1.386 (4)
O5—C13	1.207 (3)	C8—C9	1.383 (4)
N1—C1	1.321 (3)	C9—C10	1.382 (4)
N1—C2	1.370 (3)	C9—C13	1.496 (4)
C1—N1^{i}	1.321 (3)	C10—C11	1.380 (5)
C2—C3	1.367 (4)	C11—C12	1.378 (4)
C2—C2^{i}	1.391 (5)		
C6—O3—C7	118.8 (2)	O3—C7—C12	124.3 (2)
C1—N1—C2	108.9 (2)	C8—C7—C12	119.9 (3)
N1—C2—C3	131.4 (3)	C7—C8—C9	119.7 (3)
C3—C2—C2^{i}	122.3 (2)	C8—C9—C10	120.4 (3)
N1—C2—C2^{i}	106.3 (2)	C10—C9—C13	118.7 (2)
C2—C3—C4	115.7 (3)	C8—C9—C13	120.9 (3)
C3—C4—C4^{i}	121.9 (2)	C9—C10—C11	119.4 (3)
O1—C5—O2	123.8 (3)	C7—C12—C11	119.6 (3)
O1—C5—C6	121.6 (2)	C10—C11—C12	120.9 (3)
O2—C5—C6	114.6 (3)	O5—C13—O4	124.2 (3)
O3—C6—C5	108.9 (2)	O4—C13—C9	113.7 (2)
O3—C7—C8	115.7 (2)	O5—C13—C9	122.1 (3)

Symmetry code: (i) $2 - x, y, \frac{3}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4O···O1^{ii}	0.85 (1)	1.91 (1)	2.762 (3)	176 (4)
N1—H1N···O1	0.85 (1)	2.30 (2)	3.082 (3)	152 (4)
N1—H1N···O5^{ii}	0.85 (1)	2.39 (4)	2.914 (2)	120 (4)
O2—H2O···O2^{iii}	1.242 (2)	1.242 (2)	2.484 (2)	180

Symmetry codes: (ii) $1 - x, 2 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$.

The amino and carboxyl H atoms were located and refined with a distance restraint of 0.85 (1) Å. For the acid H atom that lies on an inversion center, only the displacement parameter was refined. Other H atoms were placed in calculated positions and treated as riding atoms [aromatic C—H = 0.93 Å and aliphatic C—H = 0.97 Å; $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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