

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Triclinic modification of diaquabis(5-carboxy-1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)iron(II)

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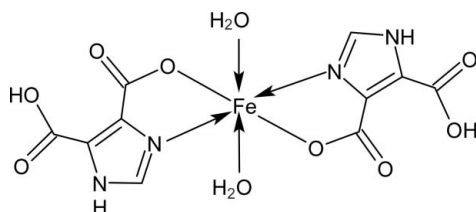
Received 12 June 2012; accepted 11 July 2012

 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.041; wR factor = 0.075; data-to-parameter ratio = 13.7.

The title compound, $[Fe(C_5H_3N_2O_4)_2(H_2O)_2]$, is a triclinic modification of a monoclinic form recently reported by Du *et al.* [*Acta Cryst.* (2011), **E67**, m997]. The Fe^{II} ion lies at an inversion center and is coordinated by two N and two O atoms from two 5-carboxy-1*H*-imidazole-4-carboxylate ligands in *trans* positions, together with two water molecules, completing a slightly distorted octahedral coordination. Intermolecular $N-H \cdots O$ hydrogen bonding between the N–H group of the imidazole ring and the deprotonated carboxylate group builds a chain of 5-carboxy-1*H*-imidazole-4-carboxylate anions along the [101] direction. The water molecules form intermolecular hydrogen bonds to O–C and O=C sites of the carboxylate group in adjacent layers.

Related literature

For the structural diversity of the coordination architecture of the metal complexes of 4,5-imidazolecarboxylic acid, see Shimizu *et al.* (2004); Fang & Zhang (2006). For the isotopic Co analog, see: Li *et al.* (2011). For the coexisting phase, see Yakubovich *et al.* (1995). For the monoclinic form, see: Du *et al.* (2011).



Experimental

Crystal data

$[Fe(C_5H_3N_2O_4)_2(H_2O)_2]$
 $M_r = 402.08$
 Triclinic, $P\bar{1}$
 $a = 4.9290$ (5) Å
 $b = 6.4258$ (6) Å
 $c = 12.2812$ (10) Å
 $\alpha = 78.161$ (3)°
 $\beta = 85.175$ (3)°
 $\gamma = 72.776$ (4)°
 $V = 363.52$ (6) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.10$ mm⁻¹
 $T = 298$ K
 $0.15 \times 0.13 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 Absorption correction: empirical (using intensity measurements) (*ABSCOR*; Higashi, 1995)
 $T_{min} = 0.852$, $T_{max} = 0.898$
 3655 measured reflections
 1668 independent reflections
 1066 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.075$
 $S = 0.92$
 1668 reflections
 122 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.30$ e Å⁻³
 $\Delta\rho_{min} = -0.34$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O5-H1W \cdots O3^i$	0.86 (3)	1.86 (3)	2.705 (3)	165 (3)
$O5-H2W \cdots O4^{ii}$	0.79 (3)	1.95 (3)	2.702 (3)	158 (3)
$N2-H2A \cdots O1^{iii}$	0.86	1.95	2.767 (3)	157
$O2-H2 \cdots O3$	0.82	1.85	2.665 (3)	174

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

This study was supported financially by the Inter-University Cooperative Research Program of the Institute for Materials Research, Tohoku University (proposal No. 11 K0091).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2571).

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supporting information

Acta Cryst. (2012). E68, m1093–m1094 [https://doi.org/10.1107/S1600536812031753]

Triclinic modification of diaquabis(5-carboxy-1*H*-imidazole-4-carboxylato- κ^2N^3, O^4)iron(II)

Eriko Ohshima, Kazuki Yoshida, Kazumasa Sugiyama and Hidehiro Uekusa

S1. Comment

A number of studies on transition metal complexes with carboxylate ligands are reported in the literature. Recently, imidazole dicarboxylate has been recognized as an efficient building block, since it shows two different coordination modes to bridge or chelate metals through the carboxyl oxygen atoms and heterocyclic nitrogen donor. The crystal of diaquabis(5-carboxy-1*H*-imidazole-4-carboxylato- κ^2N^3, O^4)iron(II) is isostructural with Co analog 4,5-dicarboxyimidazole complexes (Li *et al.*, 2011). Iron(II) ion lies at the inversion center that is coordinated by two 1*H*-imidazole-4,5-dicarboxylate monoanionic ligands at the *trans* positions and two water molecules in a distorted octahedral geometry. A previous report described a monoclinic metal complex with a similar chemical composition (Du *et al.*, 2011). This structural diversity is attributed to the different types of coordination architectures of hydrogen bonding between molecules. The intermolecular hydrogen bonding between the N—H site of an imidazole ring and C=O site of a deprotonated carboxylate in the title compound builds a unique chain of 5-carboxy-1*H*-imidazole-4-carboxylate anion. The chain structures are further linked into a three-dimensional supermolecular framework through O—H \cdots O hydrogen bonding interactions. The average distance of Fe—O agrees well with that of the monoclinic phase. Nevertheless, the average distance of Fe—N (2.165 Å) is longer than that in the monoclinic analog (2.147 Å).

S2. Experimental

A mixture of FeSO₄·7H₂O (13.33 mmol), 4,5-imidazoledicarboxamide (22.21 mmol), 85.0% H₃PO₄ (8.89 mmol), and H₂O (8 ml) was placed in a 30 ml Teflon beaker. It was sealed in a stainless-steel reactor, heated to 453 K for 96 h under autogenous pressure, and then, slowly cooled to room temperature. Pale-yellow block crystals of the title complex were isolated, washed with distilled water, and dried in air. It may be added that NH₄FePO₄·H₂O: see Yakubovich *et al.* (1995), Pale-green plate crystals were also crystallized in the present synthetic condition. This supports the hydrolysis of the 4,5-imidazoledicarboxamide during the synthesis.

S3. Refinement

H atoms attached to C and N atoms were placed at calculated positions (C—H = 0.93 Å, N—H = 0.86 Å) and refined as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The carboxy H was located at the idealized position (O—H = 0.82 Å) and refined as a riding atom with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. On the other hand, H atoms of water molecules were located in a difference map, and their positions were subsequently refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

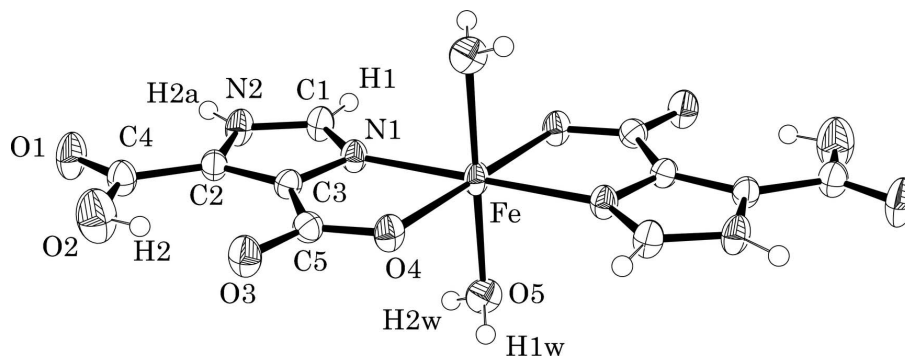


Figure 1

The molecular structure with displacement ellipsoids drawn at the 50% probability level.

Diaquabis(5-carboxy-1H-imidazole-4-carboxylato- κ^2N^3,O^4)iron(II)

Crystal data

$[\text{Fe}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$

$M_r = 402.08$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 4.9290$ (5) Å

$b = 6.4258$ (6) Å

$c = 12.2812$ (10) Å

$\alpha = 78.161$ (3)°

$\beta = 85.175$ (3)°

$\gamma = 72.776$ (4)°

$V = 363.52$ (6) Å³

$Z = 1$

$F(000) = 204$

$D_x = 1.837$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 3918 reflections

$\theta = 3.4\text{--}30.5^\circ$

$\mu = 1.10$ mm⁻¹

$T = 298$ K

Block, yellow

$0.15 \times 0.13 \times 0.10$ mm

Data collection

Rigaku R-AXIS RAPID

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 100 pixels mm⁻¹

ω scans

Absorption correction: empirical (using

intensity measurements)

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.852$, $T_{\max} = 0.898$

3655 measured reflections

1668 independent reflections

1066 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -6 \rightarrow 6$

$k = -8 \rightarrow 8$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.075$

$S = 0.92$

1668 reflections

122 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.30$ e Å⁻³

$\Delta\rho_{\min} = -0.34$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors (gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.0000	0.0000	0.0000	0.0224 (2)
O5	0.3576 (5)	-0.2580 (4)	0.06771 (17)	0.0314 (5)
H1W	0.297 (7)	-0.370 (6)	0.097 (2)	0.047*
H2W	0.489 (7)	-0.278 (6)	0.026 (3)	0.047*
N1	0.1698 (5)	-0.0023 (4)	-0.16828 (18)	0.0237 (5)
C1	0.3247 (6)	0.0920 (5)	-0.2439 (2)	0.0262 (7)
H1	0.4099	0.1967	-0.2323	0.031*
N2	0.3439 (5)	0.0184 (4)	-0.33916 (18)	0.0277 (6)
H2A	0.4346	0.0598	-0.3986	0.033*
C2	0.1936 (6)	-0.1351 (5)	-0.3258 (2)	0.0233 (7)
C3	0.0869 (6)	-0.1468 (4)	-0.2178 (2)	0.0216 (6)
C4	0.1805 (6)	-0.2443 (5)	-0.4200 (2)	0.0279 (7)
O1	0.3050 (5)	-0.2040 (4)	-0.50906 (15)	0.0409 (6)
O2	0.0250 (6)	-0.3870 (4)	-0.40319 (18)	0.0551 (7)
H2	-0.0479	-0.3917	-0.3405	0.083*
C5	-0.0966 (6)	-0.2761 (5)	-0.1514 (2)	0.0236 (6)
O3	-0.1770 (4)	-0.4089 (3)	-0.19419 (15)	0.0328 (5)
O4	-0.1626 (4)	-0.2417 (3)	-0.05321 (14)	0.0262 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0257 (4)	0.0281 (4)	0.0170 (3)	-0.0135 (3)	0.0060 (3)	-0.0062 (3)
O5	0.0304 (14)	0.0328 (14)	0.0320 (12)	-0.0157 (12)	0.0077 (9)	-0.0019 (10)
N1	0.0283 (14)	0.0267 (14)	0.0211 (11)	-0.0140 (12)	0.0014 (10)	-0.0070 (10)
C1	0.0309 (18)	0.0317 (18)	0.0225 (14)	-0.0184 (15)	0.0019 (13)	-0.0067 (13)
N2	0.0314 (15)	0.0371 (16)	0.0195 (11)	-0.0195 (13)	0.0077 (10)	-0.0058 (11)
C2	0.0284 (17)	0.0243 (17)	0.0194 (14)	-0.0103 (14)	0.0006 (12)	-0.0056 (12)
C3	0.0225 (16)	0.0235 (16)	0.0191 (13)	-0.0078 (14)	0.0012 (11)	-0.0034 (12)
C4	0.0343 (19)	0.0304 (18)	0.0244 (16)	-0.0168 (16)	0.0028 (13)	-0.0077 (13)
O1	0.0533 (16)	0.0563 (16)	0.0234 (11)	-0.0307 (14)	0.0124 (11)	-0.0134 (11)
O2	0.073 (2)	0.0626 (18)	0.0436 (14)	-0.0405 (16)	0.0158 (13)	-0.0184 (14)
C5	0.0250 (17)	0.0234 (17)	0.0239 (15)	-0.0083 (14)	-0.0014 (12)	-0.0052 (13)
O3	0.0458 (14)	0.0345 (13)	0.0281 (10)	-0.0261 (12)	0.0047 (10)	-0.0087 (9)
O4	0.0302 (12)	0.0313 (12)	0.0218 (10)	-0.0179 (11)	0.0088 (9)	-0.0057 (9)

Geometric parameters (\AA , $^\circ$)

Fe1—O5	2.121 (2)	C1—H1	0.9300
Fe1—O5 ⁱ	2.121 (2)	N2—C2	1.377 (3)
Fe1—N1 ⁱ	2.165 (2)	N2—H2A	0.8600
Fe1—N1	2.165 (2)	C2—C3	1.380 (3)
Fe1—O4 ⁱ	2.1732 (16)	C2—C4	1.487 (3)
Fe1—O4	2.1732 (16)	C3—C5	1.489 (4)
O5—H1W	0.86 (3)	C4—O1	1.226 (3)
O5—H2W	0.79 (3)	C4—O2	1.335 (3)
N1—C1	1.317 (3)	O2—H2	0.8200
N1—C3	1.377 (3)	C5—O3	1.257 (3)
C1—N2	1.336 (3)	C5—O4	1.269 (3)
O5—Fe1—O5 ⁱ	180.00 (11)	N1—C1—N2	111.5 (2)
O5—Fe1—N1 ⁱ	87.70 (9)	N1—C1—H1	124.3
O5 ⁱ —Fe1—N1 ⁱ	92.30 (9)	N2—C1—H1	124.3
O5—Fe1—N1	92.30 (9)	C1—N2—C2	108.2 (2)
O5 ⁱ —Fe1—N1	87.70 (9)	C1—N2—H2A	125.9
N1 ⁱ —Fe1—N1	180.00 (16)	C2—N2—H2A	125.9
O5—Fe1—O4 ⁱ	90.06 (7)	N2—C2—C3	105.0 (2)
O5 ⁱ —Fe1—O4 ⁱ	89.94 (7)	N2—C2—C4	119.4 (2)
N1 ⁱ —Fe1—O4 ⁱ	76.79 (7)	C3—C2—C4	135.6 (2)
N1—Fe1—O4 ⁱ	103.21 (7)	N1—C3—C2	109.3 (2)
O5—Fe1—O4	89.94 (7)	N1—C3—C5	118.0 (2)
O5 ⁱ —Fe1—O4	90.06 (7)	C2—C3—C5	132.7 (2)
N1 ⁱ —Fe1—O4	103.21 (7)	O1—C4—O2	121.8 (2)
N1—Fe1—O4	76.79 (7)	O1—C4—C2	121.5 (2)
O4 ⁱ —Fe1—O4	180.00 (12)	O2—C4—C2	116.7 (2)
Fe1—O5—H1W	107 (2)	C4—O2—H2	109.5
Fe1—O5—H2W	113 (3)	O3—C5—O4	124.3 (3)
H1W—O5—H2W	117 (3)	O3—C5—C3	119.6 (2)
C1—N1—C3	106.0 (2)	O4—C5—C3	116.1 (2)
C1—N1—Fe1	141.85 (18)	C5—O4—Fe1	116.99 (16)
C3—N1—Fe1	112.14 (17)		

Symmetry code: (i) $-x, -y, -z$.Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H1W \cdots O3 ⁱⁱ	0.86 (3)	1.86 (3)	2.705 (3)	165 (3)
O5—H2W \cdots O4 ⁱⁱⁱ	0.79 (3)	1.95 (3)	2.702 (3)	158 (3)
N2—H2A \cdots O1 ^{iv}	0.86	1.95	2.767 (3)	157
O2—H2 \cdots O3	0.82	1.85	2.665 (3)	174

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