metal-organic compounds

Poly[(μ₃-nicotinato-κ^3O:O′:N)-(μ₂-nicotinato-κ^3O,O′:N)iron(II)]

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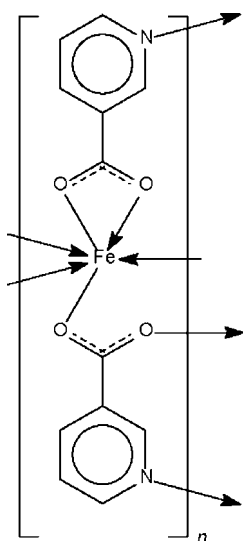Correspondence e-mail: seikweng@um.edu.my

In the crystal structure of the title compound, $[Fe(C_6H_4NO_2)_2]_n$, one nicotinate group $O,O′$-chelates one Fe atom and binds through the N atom to the other Fe atom; the second nicotinate group bridges three Fe atoms through the N and two O atoms. The μ_2- and μ_3-bridging modes of the two nicotinate groups result in a polymeric three-dimensional network structure. The Fe atom shows octahedral coordination geometry but one of the Fe—O bonds is somewhat long [2.522 (2) Å].

Related literature

For zwitterionic tetraaquadi(nicotinato-κN)iron(II), see: Liang *et al.* (2005).

Experimental

Crystal data

$[Fe(C_6H_4NO_2)_2]$
M_r = 300.05

Monoclinic, $P2_1/n$
a = 10.8771 (7) Å

b = 9.6066 (6) Å
c = 12.7284 (8) Å
β = 111.619 (1)°
V = 1236.5 (1) Å³
Z = 4

Mo $K\alpha$ radiation
μ = 1.23 mm⁻¹
T = 295 (2) K
0.41 × 0.34 × 0.25 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.564, T_{max} = 0.749

7255 measured reflections
2762 independent reflections
2428 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.078
S = 1.02
2762 reflections

172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å⁻³
$\Delta\rho_{min}$ = −0.27 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	2.522 (2)	Fe1—O4ⁱ	2.061 (1)
Fe1—O2	2.072 (1)	Fe1—N1ⁱⁱ	2.212 (1)
Fe1—O3	2.012 (1)	Fe1—N2ⁱⁱⁱ	2.224 (1)
O1—Fe1—O2	56.18 (5)	O2—Fe1—N2ⁱⁱⁱ	90.93 (5)
O1—Fe1—O3	96.95 (5)	O3—Fe1—O4ⁱ	120.67 (6)
O1—Fe1—O4ⁱ	142.30 (5)	O3—Fe1—N1ⁱⁱ	88.50 (5)
O1—Fe1—N1ⁱⁱ	89.36 (5)	O3—Fe1—N2ⁱⁱⁱ	89.17 (5)
O1—Fe1—N2ⁱⁱⁱ	93.18 (5)	O4ⁱ—Fe1—N1ⁱⁱ	89.39 (6)
O2—Fe1—O3	153.10 (6)	O4ⁱ—Fe1—N2ⁱⁱⁱ	89.83 (6)
O2—Fe1—O4ⁱ	86.23 (5)	N1ⁱⁱ—Fe1—N2ⁱⁱⁱ	176.74 (5)
O2—Fe1—N1ⁱⁱ	92.17 (5)		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001) and *OLEX* (Dolomanov *et al.*, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2008).

References

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Dolomanov, O. V., Blake, A. J., Champness, N. R. & Schröder, M. (2003). *J. Appl. Cryst.* **36**, 1283–1284.
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Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
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supporting information

Poly[(*μ*₃-nicotinato-*κ*³*O:O′:N*)(*μ*₂-nicotinato-*κ*³*O,O′:N*)iron(II)]

Seik Weng Ng

S1. Comment

The crystal structures of a large number of divalent metal dinicotinates are known; the compounds exists as water-coordinated compounds in which the nicotinate ion binds through the aromatic N atom and not through the carboxyl group, as exemplified by tetraaquadinicotinatoiron(II). The report on this compound lists the crystal structures of tetra-aquametal dinicotinates (Liang *et al.*, 2005). Tetraaquadinicotinatoiron is synthesized by reaction of the metal salt with nicotinic acid under aqueous conditions; under hydrothermal conditions, the synthesis has yielded the anhydrous compound (I). Iron dinicotinate (Fig. 1) has the nicotinate group engaged into two types of bridging interactions; one group *O,O′*-chelate to one Fe atom and binds through the N atom to the other Fe atom; the second nicotinate group bridges three Fe atoms through the N and two O atoms. The μ_2 and μ_3 bridging modes of the two nicotinate groups result in a polymeric three-dimensional network structure (Fig. 2). The Fe atom shows the common octahedral coordination geometry but one of the Fe–O bonds is somewhat long (Table 1).

S2. Experimental

Iron powder (0.056 g, 1 mmol), nicotinic acid (0.218 g 2 mmol) and water (10 ml) heated in a 23-ml, Teflon-lined, Parr bomb at 423 K for 3 days. The bomb was cooled to room temperature at a rate of 10 K per min to give yellow block-shaped crystals (in 10% yield based on nicotinic acid rate of 10 ºC.h-1. The yellow block crystals of iron dinicoinate were obtained (yield 8.2% based on nicotinic acid).

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.93 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2*U*(C).
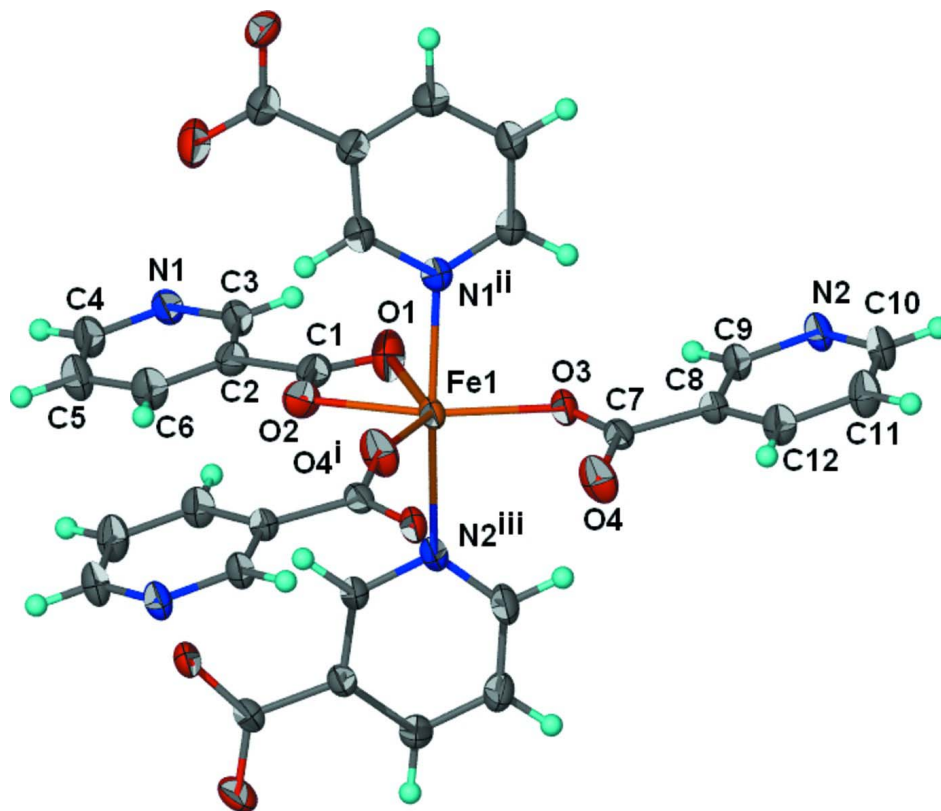
Figure 1

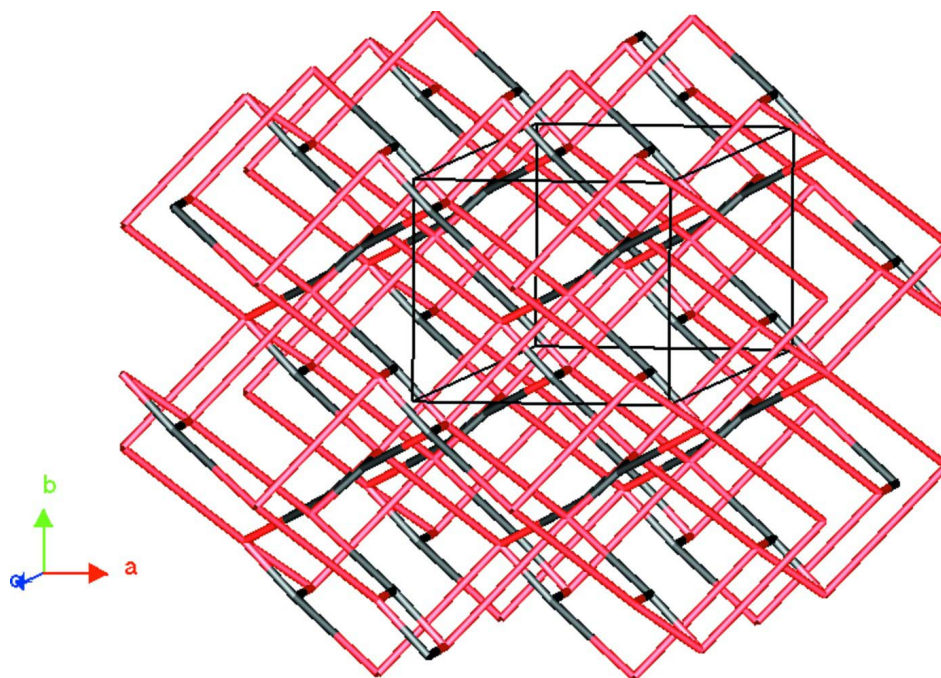50% Probability thermal ellipsoid plot illustrating the octahedral geometry at iron.

Figure 2

OLEX (Dolomanov *et al.*, 2003) illustration of the three-dimensional network motif.

Poly[(μ_3-nicotinato-κ^3O:O':N)(μ_2-nicotinato- κ^3O,O':N)iron(II)]

Crystal data

[Fe($C_6H_4NO_2$)$_2$]	$F(000) = 608$
$M_r = 300.05$	$D_x = 1.612$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 6064 reflections
$a = 10.8771$ (7) Å	$\theta = 2.1–27.5°$
$b = 9.6066$ (6) Å	$\mu = 1.23$ mm^{-1}
$c = 12.7284$ (8) Å	$T = 295$ K
$\beta = 111.619$ (1)°	Block, yellow
$V = 1236.5$ (1) Å^3	$0.41 \times 0.34 \times 0.25$ mm
$Z = 4$	

Data collection

Bruker APEX diffractometer	7255 measured reflections
Radiation source: fine-focus sealed tube	2762 independent reflections
Graphite monochromator	2428 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.018$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
	$h = -14\rightarrow14$
	$k = -10\rightarrow12$
$T_{min} = 0.564$, $T_{max} = 0.749$	$l = -13\rightarrow16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.078$	
$S = 1.02$	H-atom parameters constrained
2762 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.2265P]$ where $P = (F_o^2 + 2F_c^2)/3$
172 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.24$ e Å^{-3}
	$\Delta\rho_{min} = -0.27$ e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
Fe1	0.40603 (2)	0.37707 (2)	0.580119 (18)	0.02707 (10)
O1	0.28044 (15)	0.19952 (16)	0.64714 (12)	0.0540 (4)
O2	0.43525 (13)	0.34442 (14)	0.74858 (11)	0.0398 (3)
O3	0.32118 (11)	0.33429 (14)	0.41409 (10)	0.0345 (3)
O4	0.45693 (13)	0.46511 (14)	0.36328 (12)	0.0477 (3)
N1	0.25364 (13)	0.02956 (15)	0.94060 (12)	0.0335 (3)
N2	0.06748 (13)	0.27149 (15)	0.09200 (12)	0.0335 (3)
C1	0.35420 (18)	0.24585 (18)	0.73955 (15)	0.0371 (4)
C2	0.35386 (17)	0.18565 (18)	0.84835 (14)	0.0336 (4)
C3	0.25803 (17)	0.09027 (18)	0.84724 (15)	0.0344 (4)

H3	0.1932	0.0671	0.7780	0.041*
C4	0.34759 (18)	0.0657 (2)	1.03903 (15)	0.0396 (4)
H4	0.3462	0.0246	1.1047	0.048*
C5	0.4460 (2)	0.1601 (2)	1.04838 (16)	0.0450 (5)
H5	0.5090	0.1824	1.1187	0.054*
C6	0.44980 (18)	0.2211 (2)	0.95150 (16)	0.0415 (4)
H6	0.5156	0.2849	0.9554	0.050*
C7	0.35595 (15)	0.39427 (16)	0.34127 (14)	0.0283 (3)
C8	0.26579 (15)	0.37708 (15)	0.22048 (14)	0.0281 (3)
C9	0.15745 (16)	0.29047 (17)	0.19585 (13)	0.0314 (3)
H9	0.1464	0.2424	0.2552	0.038*
C10	0.08654 (19)	0.3417 (2)	0.00799 (15)	0.0400 (4)
H10	0.0251	0.3306	−0.0651	0.048*
C11	0.19213 (19)	0.4291 (2)	0.02432 (15)	0.0432 (4)
H11	0.2013	0.4753	−0.0366	0.052*
C12	0.28458 (18)	0.44749 (18)	0.13239 (15)	0.0368 (4)
H12	0.3572	0.5054	0.1456	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.02436 (14)	0.03310 (15)	0.01968 (14)	−0.00138 (8)	0.00333 (10)	−0.00096 (8)
O1	0.0695 (10)	0.0593 (9)	0.0300 (7)	−0.0046 (8)	0.0145 (7)	0.0019 (6)
O2	0.0405 (7)	0.0448 (7)	0.0379 (7)	0.0017 (6)	0.0188 (6)	0.0113 (5)
O3	0.0304 (6)	0.0479 (7)	0.0207 (6)	−0.0014 (5)	0.0042 (5)	−0.0011 (5)
O4	0.0393 (7)	0.0507 (8)	0.0417 (8)	−0.0193 (6)	0.0014 (6)	−0.0023 (6)
N1	0.0301 (7)	0.0397 (8)	0.0282 (7)	−0.0009 (6)	0.0080 (6)	0.0040 (6)
N2	0.0311 (7)	0.0408 (8)	0.0225 (7)	−0.0059 (6)	0.0027 (6)	0.0003 (6)
C1	0.0419 (9)	0.0396 (9)	0.0332 (9)	0.0092 (8)	0.0176 (8)	0.0055 (7)
C2	0.0358 (9)	0.0359 (9)	0.0311 (9)	0.0018 (7)	0.0146 (7)	0.0027 (7)
C3	0.0331 (8)	0.0396 (9)	0.0267 (8)	0.0007 (7)	0.0065 (7)	0.0021 (7)
C4	0.0389 (9)	0.0504 (11)	0.0267 (9)	−0.0055 (8)	0.0089 (7)	0.0053 (8)
C5	0.0426 (10)	0.0566 (12)	0.0285 (9)	−0.0122 (9)	0.0045 (8)	0.0005 (8)
C6	0.0403 (9)	0.0462 (10)	0.0368 (10)	−0.0110 (8)	0.0127 (8)	0.0018 (8)
C7	0.0255 (8)	0.0286 (8)	0.0262 (8)	0.0026 (6)	0.0044 (6)	−0.0032 (6)
C8	0.0270 (8)	0.0311 (8)	0.0240 (8)	−0.0006 (6)	0.0066 (6)	−0.0023 (6)
C9	0.0305 (8)	0.0383 (9)	0.0224 (8)	−0.0044 (7)	0.0061 (6)	0.0015 (6)
C10	0.0433 (10)	0.0458 (10)	0.0222 (8)	−0.0046 (8)	0.0017 (7)	0.0014 (7)
C11	0.0519 (11)	0.0481 (10)	0.0274 (9)	−0.0099 (9)	0.0121 (8)	0.0059 (8)
C12	0.0378 (9)	0.0398 (9)	0.0313 (9)	−0.0093 (7)	0.0109 (7)	0.0003 (7)

Geometric parameters (Å, º)

Fe1—O1	2.522 (2)	C2—C3	1.384 (2)
Fe1—O2	2.072 (1)	C2—C6	1.385 (3)
Fe1—O3	2.012 (1)	C3—H3	0.9300
Fe1—O4[i]	2.061 (1)	C4—C5	1.375 (3)
Fe1—N1[ii]	2.212 (1)	C4—H4	0.9300

Fe1—N2[iii]	2.224 (1)	C5—C6	1.379 (3)
O1—C1	1.237 (2)	C5—H5	0.9300
O2—C1	1.270 (2)	C6—H6	0.9300
O3—C7	1.262 (2)	C7—C8	1.497 (2)
O4—C7	1.233 (2)	C8—C9	1.381 (2)
O4—Fe1[i]	2.0611 (12)	C8—C12	1.388 (2)
N1—C4	1.338 (2)	C9—H9	0.9300
N1—C3	1.340 (2)	C10—C11	1.375 (3)
N1—Fe1[iv]	2.2124 (14)	C10—H10	0.9300
N2—C9	1.336 (2)	C11—C12	1.384 (2)
N2—C10	1.343 (2)	C11—H11	0.9300
N2—Fe1[v]	2.2243 (14)	C12—H12	0.9300
C1—C2	1.502 (2)		
O1—Fe1—O2	56.18 (5)	N1—C3—C2	123.49 (16)
O1—Fe1—O3	96.95 (5)	N1—C3—H3	118.3
O1—Fe1—O4[i]	142.30 (5)	C2—C3—H3	118.3
O1—Fe1—N1[ii]	89.36 (5)	N1—C4—C5	123.64 (17)
O1—Fe1—N2[iii]	93.18 (5)	N1—C4—H4	118.2
O2—Fe1—O3	153.10 (6)	C5—C4—H4	118.2
O2—Fe1—O4[i]	86.23 (5)	C4—C5—C6	118.78 (18)
O2—Fe1—N1[ii]	92.17 (5)	C4—C5—H5	120.6
O2—Fe1—N2[iii]	90.93 (5)	C6—C5—H5	120.6
O3—Fe1—O4[i]	120.67 (6)	C5—C6—C2	118.87 (17)
O3—Fe1—N1[ii]	88.50 (5)	C5—C6—H6	120.6
O3—Fe1—N2[iii]	89.17 (5)	C2—C6—H6	120.6
O4[i]—Fe1—N1[ii]	89.39 (6)	O4—C7—O3	124.60 (16)
O4[i]—Fe1—N2[iii]	89.83 (6)	O4—C7—C8	119.06 (15)
N1[ii]—Fe1—N2[iii]	176.74 (5)	O3—C7—C8	116.33 (14)
C1—O1—Fe1	80.56 (11)	C9—C8—C12	118.53 (15)
C1—O2—Fe1	100.52 (11)	C9—C8—C7	118.75 (15)
C7—O3—Fe1	122.17 (11)	C12—C8—C7	122.70 (15)
C7—O4—Fe1[i]	162.57 (13)	N2—C9—C8	124.03 (15)
C4—N1—C3	116.93 (15)	N2—C9—H9	118.0
C4—N1—Fe1[iv]	125.34 (12)	C8—C9—H9	118.0
C3—N1—Fe1[iv]	117.73 (11)	N2—C10—C11	123.46 (16)
C9—N2—C10	116.58 (14)	N2—C10—H10	118.3
C9—N2—Fe1[v]	115.27 (11)	C11—C10—H10	118.3
C10—N2—Fe1[v]	128.13 (12)	C10—C11—C12	119.27 (17)
O1—C1—O2	122.67 (17)	C10—C11—H11	120.4
O1—C1—C2	121.14 (17)	C12—C11—H11	120.4
O2—C1—C2	116.18 (16)	C11—C12—C8	118.12 (16)
C3—C2—C6	118.28 (16)	C11—C12—H12	120.9
C3—C2—C1	120.21 (16)	C8—C12—H12	120.9
C6—C2—C1	121.49 (16)		
O3—Fe1—O1—C1	177.00 (11)	C1—C2—C3—N1	178.18 (15)
O4[i]—Fe1—O1—C1	−6.40 (16)	C3—N1—C4—C5	0.0 (3)

O2—Fe1—O1—C1	−1.54 (10)	Fe1ⁱᵛ—N1—C4—C5	179.39 (16)
N1ⁱⁱ—Fe1—O1—C1	−94.59 (11)	N1—C4—C5—C6	−0.4 (3)
N2ⁱⁱⁱ—Fe1—O1—C1	87.45 (11)	C4—C5—C6—C2	0.4 (3)
O3—Fe1—O2—C1	−1.69 (18)	C3—C2—C6—C5	0.1 (3)
O4ⁱ—Fe1—O2—C1	178.53 (11)	C1—C2—C6—C5	−178.59 (17)
N1ⁱⁱ—Fe1—O2—C1	89.28 (11)	Fe1ⁱ—O4—C7—O3	−68.9 (5)
N2ⁱⁱⁱ—Fe1—O2—C1	−91.70 (11)	Fe1ⁱ—O4—C7—C8	110.7 (4)
O1—Fe1—O2—C1	1.51 (10)	Fe1—O3—C7—O4	12.9 (2)
O4ⁱ—Fe1—O3—C7	5.56 (14)	Fe1—O3—C7—C8	−166.66 (10)
O2—Fe1—O3—C7	−174.18 (11)	O4—C7—C8—C9	175.90 (15)
N1ⁱⁱ—Fe1—O3—C7	93.97 (13)	O3—C7—C8—C9	−4.5 (2)
N2ⁱⁱⁱ—Fe1—O3—C7	−83.75 (13)	O4—C7—C8—C12	−5.9 (2)
O1—Fe1—O3—C7	−176.85 (12)	O3—C7—C8—C12	173.73 (15)
Fe1—O1—C1—O2	2.49 (16)	C10—N2—C9—C8	0.4 (3)
Fe1—O1—C1—C2	−176.46 (16)	Fe1ᵛ—N2—C9—C8	179.22 (13)
Fe1—O2—C1—O1	−3.0 (2)	C12—C8—C9—N2	−1.1 (3)
Fe1—O2—C1—C2	175.95 (12)	C7—C8—C9—N2	177.20 (15)
O1—C1—C2—C3	−9.1 (3)	C9—N2—C10—C11	0.3 (3)
O2—C1—C2—C3	171.91 (16)	Fe1ᵛ—N2—C10—C11	−178.38 (15)
O1—C1—C2—C6	169.55 (18)	N2—C10—C11—C12	−0.2 (3)
O2—C1—C2—C6	−9.5 (2)	C10—C11—C12—C8	−0.5 (3)
C4—N1—C3—C2	0.4 (3)	C9—C8—C12—C11	1.1 (3)
Fe1ⁱᵛ—N1—C3—C2	−178.97 (13)	C7—C8—C12—C11	−177.12 (16)
C6—C2—C3—N1	−0.5 (3)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iii) *x*+1/2, −*y*+1/2, *z*+1/2; (iv) −*x*+1/2, *y*−1/2, −*z*+3/2; (v) *x*−1/2, −*y*+1/2, *z*−1/2.