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Isotypic Mn^{II} and Fe^{II} binuclear complexes of the ligand 5,6-bis(pyridin-2-yl)-pyrazine-2,3-dicarboxylic acid

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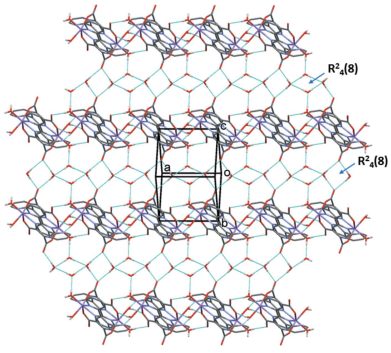
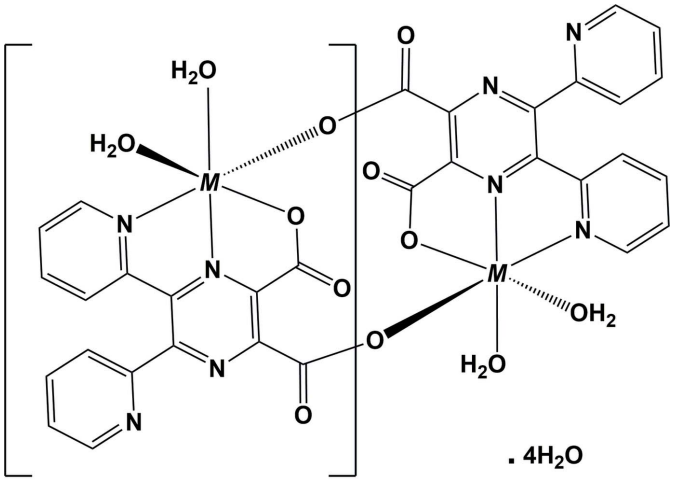
The title isotypic complexes, bis[μ-5,6-bis(pyridin-2-yl)pyrazine-2,3-dicarboxylato]-$\kappa^4N^1,O^2,N^6:O^3;\kappa^4O^3:N^1,O^2,N^6$-bis[diaquamanganese(II)] tetrahydrate, $[Mn_2(C_{16}H_8N_4O_4)_2(H_2O)_4]\cdot 4H_2O$, (I), and bis[$\mu$-5,6-bis(pyridin-2-yl)pyrazine-2,3-dicarboxylato]-$\kappa^4N^1,O^2,N^6:O^3;\kappa^4O^3:N^1,O^2,N^6$-bis[diaquairon(II)] tetrahydrate, $[Fe_2(C_{16}H_8N_4O_4)_2(H_2O)_4]\cdot 4H_2O$, (II), are, respectively, the manganese(II) and iron(II) complexes of the ligand 5,6-bis(pyridin-2-yl)-pyrazine-2,3-dicarboxylic acid. The complete molecule of each complex is generated by inversion symmetry. Each metal ion is coordinated by a pyrazine N atom, a pyridine N atom, two carboxylate O atoms, one of which is bridging, and two water O atoms. The metal atoms have MN_2O_4 coordination geometries and the complexes have a cage-like structure. In the crystals of both compounds, the complexes are linked by O—H···O and O—H···N hydrogen bonds involving the coordinating water molecules, forming chains along [100]. These chains are linked by O—H···O hydrogen bonds involving the non-coordinating water molecules, forming layers parallel to (011). The layers are linked by pairs of C—H···O hydrogen bonds and offset π–π interactions, so forming a hydrogen-bonded three-dimensional framework.

1. Chemical context

The syntheses and crystal structures of the ligand 5,6-bis-(pyridin-2-yl)pyrazine-2,3-dicarboxylic acid (**H_2L**) and three different salts, have been described by Alfonso *et al.* (2001), and it was noted that the ligand crystallizes as a zwitterion in all four compounds. The reaction of **H_2L** with $CuBr_2$ (ratio 1:2) led to the formation of a one-dimensional coordination polymer. On exposure to air, this compound loses the solvent of crystallization and four water molecules, transforming into a polymeric two-dimensional network structure (Neels *et al.*, 2003). In both cases, there are two crystallographically independent fivefold-coordinated copper atoms present, each having an almost perfect square-pyramidal geometry. Recently, we have reported on the crystal structure of the cadmium dichloride complex of ligand **H_2L**, which is a two-dimensional coordination polymer (Alfonso & Stoeckli-Evans, 2016). Herein, we describe the syntheses and crystal structures of the title isotypic binuclear complexes, (I) and (II), formed by the reaction of **H_2L** with, respectively, $MnCl_2$ and $FeCl_2$.





(I) $M = Mn^{II}$
(II) $M = Fe^{II}$

2. Structural commentary

The complete molecules of complexes (I) and (II) are generated by inversion symmetry, as shown in Figs. 1 and 2, respectively. The metal atoms are sixfold coordinated by one pyrazine N atom (N1), one pyridine N atom (N3), two water O atoms (O1*W* and O2*W*), and by two carboxylate O atoms, O1 and O3^{i} [symmetry code: (i) $-x+2, -y+2, -z+2$]. Hence, the ligand coordinates to the metal atoms in a tridentate (*N,N,O*) and a monodentate (*O*) manner. Atom O3 is bridging, so leading to the formation of a cage-like complex situated about a centre of inversion; illustrated in Fig. 3 for the Fe^{II} complex, (II). The metal–metal distances are Mn1$\cdots$Mn1^{i} *ca* 6.58 Å, while the Fe1$\cdots$Fe1^{i} distance is *ca* 6.50 Å. Selected bond lengths and angles for compounds (I) and (II), are given in Tables 1 and 2, respectively.

In complex (I), it can be seen from the carboxylate C—O bond lengths [C15—O1 and C15—O2 are 1.257 (4) and 1.243 (4) Å, respectively, and C16—O3 and C16—O4 are 1.254 (4) and 1.239 (4) Å, respectively], that the negative charge is distributed over the O–C–O groups (Table 1). The

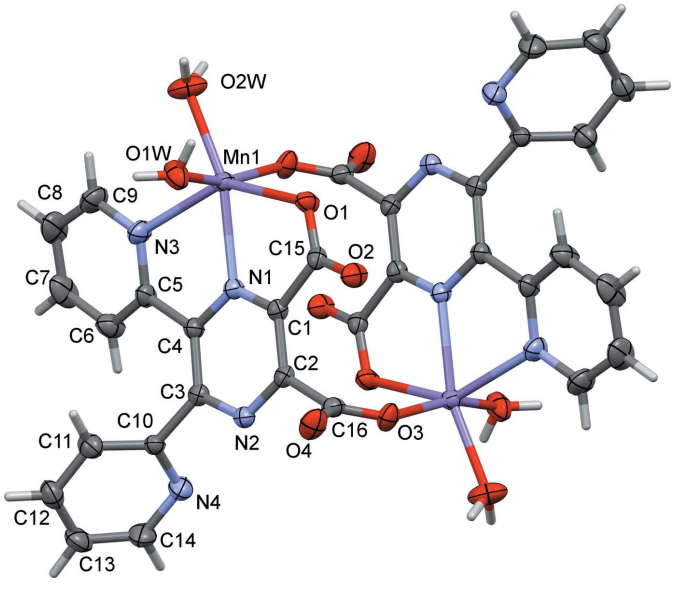


Figure 1
A view of the molecular structure of compound (I), with atom labelling. Unlabelled atoms are related to the labelled atoms by inversion symmetry ($-x+2, -y+2, -z+2$). Displacement ellipsoids are drawn at the 50% probability level. The solvate water molecules have been omitted for clarity.

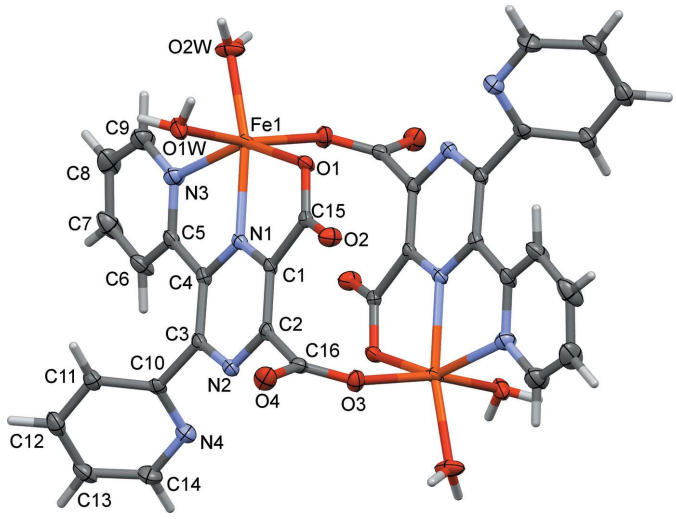


Figure 2
A view of the molecular structure of compound (II), with atom labelling. Unlabelled atoms are related to the labelled atoms by inversion symmetry ($-x+2, -y+2, -z+2$). Displacement ellipsoids are drawn at the 50% probability level. The solvate water molecules have been omitted for clarity.

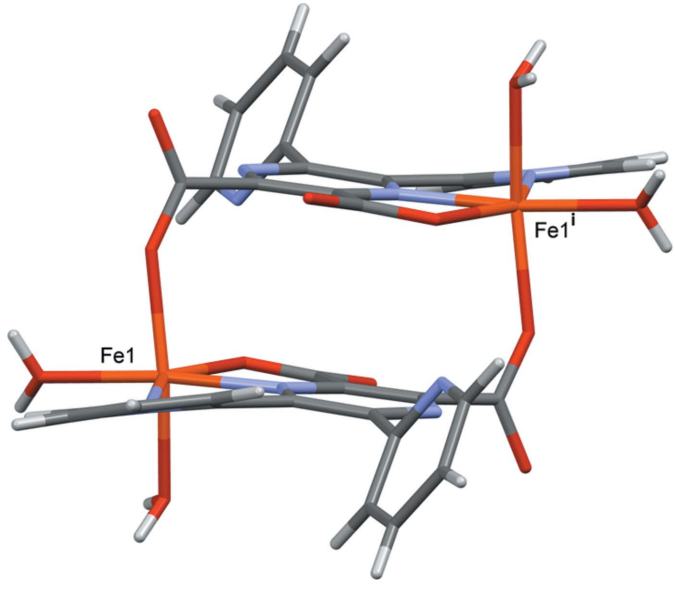


Figure 3
A view of the molecular structure of compound (II), illustrating the cage-like form of the complexes [symmetry code: (i) $-x+2, -y+2, -z+2$].

Table 1
Selected geometric parameters (Å, °) for (I).

Mn1—O3^{i}	2.139 (2)	Mn1—N3	2.311 (3)
Mn1—O1*W*	2.141 (3)	O1—C15	1.257 (4)
Mn1—O2*W*	2.148 (3)	O2—C15	1.243 (4)
Mn1—O1	2.228 (2)	O3—C16	1.254 (4)
Mn1—N1	2.242 (3)	O4—C16	1.239 (4)
O3^{i}—Mn1—O1*W*	162.15 (10)	O2*W*—Mn1—N1	163.62 (11)
O3^{i}—Mn1—O2*W*	85.00 (11)	O1—Mn1—N1	71.84 (8)
O1*W*—Mn1—O2*W*	86.92 (12)	O3^{i}—Mn1—N3	100.80 (10)
O3^{i}—Mn1—O1	89.80 (9)	O1*W*—Mn1—N3	95.57 (11)
O1*W*—Mn1—O1	81.62 (10)	O2*W*—Mn1—N3	93.71 (11)
O2*W*—Mn1—O1	124.11 (10)	O1—Mn1—N3	141.63 (9)
O3^{i}—Mn1—N1	99.80 (10)	N1—Mn1—N3	70.05 (9)
O1*W*—Mn1—N1	92.39 (11)		

Symmetry code: (i) $-x+2, -y+2, -z+2$.

Table 2
Selected geometric parameters (Å, °) for (II).

Fe1—O3^{i}	2.105 (2)	Fe1—N3	2.205 (3)
Fe1—O1*W*	2.115 (2)	O1—C15	1.271 (4)
Fe1—O2*W*	2.066 (2)	O2—C15	1.229 (4)
Fe1—O1	2.131 (2)	O3—C16	1.251 (3)
Fe1—N1	2.126 (2)	O4—C16	1.240 (4)
O3^{i}—Fe1—O1*W*	164.77 (9)	O2*W*—Fe1—N1	165.15 (10)
O3^{i}—Fe1—O2*W*	85.22 (9)	N1—Fe1—O1	74.91 (9)
O1*W*—Fe1—O2*W*	87.43 (10)	O3^{i}—Fe1—N3	99.60 (9)
O3^{i}—Fe1—O1	89.65 (8)	O1*W*—Fe1—N3	94.03 (10)
O1*W*—Fe1—O1	82.38 (9)	O2*W*—Fe1—N3	92.45 (10)
O2*W*—Fe1—O1	119.49 (10)	O1—Fe1—N3	147.49 (9)
O3^{i}—Fe1—N1	99.21 (9)	N1—Fe1—N3	72.87 (10)
O1*W*—Fe1—N1	91.27 (9)		

Symmetry code: (i) $-x+2, -y+2, -z+2$.

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1^{ii}	0.83 (2)	1.89 (2)	2.710 (4)	168 (4)
O1*W*—H1*WB*···N4^{iii}	0.84 (2)	1.91 (2)	2.750 (4)	179 (5)
O2*W*—H2*WA*···O2^{ii}	0.84 (2)	1.91 (2)	2.743 (4)	170 (5)
O2*W*—H2*WB*···O3*W*^{iv}	0.83 (2)	1.92 (3)	2.710 (4)	159 (4)
O3*W*—H3*WA*···O4*W*	0.83 (2)	2.08 (2)	2.888 (5)	163 (5)
O3*W*—H3*WB*···O4*W*^{v}	0.85 (2)	2.07 (2)	2.906 (5)	169 (5)
O4*W*—H4*WA*···O4^{vi}	0.84 (2)	2.16 (2)	3.000 (4)	175 (6)
O4*W*—H4*WB*···O4^{vii}	0.84 (2)	1.95 (2)	2.793 (4)	176 (6)
C7—H7···O3^{viii}	0.93	2.40	3.216 (5)	147
C8—H8···O2^{viii}	0.93	2.54	3.452 (4)	167

Symmetry codes: (ii) $-x+1, -y+2, -z+2$; (iii) $x-1, y, z$; (iv) $x, y+1, z$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+1, -y+1, -z+2$; (vii) $x-1, y, z-1$; (viii) $x, y, z-1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1^{ii}	0.84 (2)	1.93 (2)	2.728 (3)	160 (4)
O1*W*—H1*WB*···N4^{iii}	0.83 (2)	1.94 (2)	2.752 (3)	165 (6)
O2*W*—H2*WA*···O2^{ii}	0.87 (2)	1.83 (2)	2.694 (3)	172 (3)
O2*W*—H2*WB*···O3*W*^{iv}	0.84 (2)	1.87 (2)	2.686 (4)	165 (4)
O3*W*—H3*WA*···O4*W*	0.83 (2)	2.04 (2)	2.874 (4)	176 (6)
O3*W*—H3*WB*···O4*W*^{v}	0.84 (2)	2.03 (2)	2.866 (4)	171 (4)
O4*W*—H4*WA*···O4^{vi}	0.84 (2)	2.12 (2)	2.957 (4)	172 (5)
O4*W*—H4*WB*···O4^{vii}	0.82 (2)	1.96 (2)	2.784 (4)	178 (7)
C7—H7···O3^{viii}	0.94	2.36	3.206 (5)	149
C8—H8···O2^{viii}	0.94	2.57	3.477 (4)	162

Symmetry codes: (ii) $-x+1, -y+2, -z+2$; (iii) $x-1, y, z$; (iv) $x, y+1, z$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+1, -y+1, -z+2$; (vii) $x-1, y, z-1$; (viii) $x, y, z-1$.

Mn—$N_{pyrazine}$, Mn1—N1, bond length is 2.242 (3) Å, which is shorter than the Mn—$N_{pyridine}$, Mn1—N3, bond length of 2.311 (3) Å. The Mn1—O_{water} bond lengths [2.141 (3) and 2.148 (3) Å] are similar to the Mn—$O_{carboxylate}$, Mn1—O3^{i}, bond length of 2.139 (2) Å, while distance Mn1—O1 is longer at 2.228 (2) Å.

In complex (II), the carboxylate C—O distances [C15—O1 and C15—O2 are 1.271 (4) and 1.229 (4) Å, respectively, and C16—O3 and C16—O4 are 1.251 (3) and 1.240 (4) Å, respectively], indicate that the negative charge is centred on atom O1 for carboxylate O1–C15–O2, while for carboxylate O3–C16–O4 is appears to be distributed over the O–C–O group (Table 2). This situation is similar to that observed for the coordinating carboxylate groups in the Cd^{II} two-dimensional coordination polymer involving ligand **H_2L**, mentioned above. The Fe—$N_{pyrazine}$ bond length, Fe1—N1, is 2.126 (2) Å, which is slightly shorter than the Fe—$N_{pyridine}$, Fe1—N3, bond length of 2.205 (3) Å. The Fe1—O_{water} bond lengths [2.115 (2) and 2.066 (2) Å] are similar to the Fe1—$O_{carboxylate}$ bond lengths [2.131 (2) and 2.139 (2) Å].

The geometry of the sixfold coordinated metal atoms can best be described as a distorted octahedron, with atoms O1,N3,O1*W*,O3^{i} in the equatorial plane and atoms O2*W* and N1 in the apical positions with an O2*W*—Mn1—N1 bond angle of 163.62 (11) ° (Table 1), and an O2*W*—Fe1—N1 bond angle of 165.15 (10)° (Table 2). The coordinating pyridine ring (N3/C5–C9) and the carboxylate group (O1/O2/C15) are inclined to the mean plane of the pyrazine ring by 18.57 (17) and 7.8 (4)°, respectively, in (I) and by 14.71 (16) and 7.4 (4)°, respectively, in (II). The non-coordinating pyridine ring (N4/C10–C14) and the second coordinating carboxylate group (O3/O4/C16) are inclined to the mean plane of the pyrazine ring by 65.42 (16) and 80.64 (4)°, respectively, in (I) and by 64.59 (16) and 79.4 (4)°, respectively, in (II). In compound (I) the two pyridine rings are inclined to one another by 57.16 (18)°, very similar to the same dihedral angle in (II), *viz.* 57.28 (17)°.

3. Supramolecular features

Details of the hydrogen-bonding interactions in the crystals of both compounds, are given in Table 3 for (I) and Table 4 for (II). In the crystals of both compounds, the complexes are linked by O—H···O and O—H···N hydrogen bonds, involving the coordinating water molecules (O1*W* and O2*W*), forming chains along [100]; illustrated in Fig. 4 for compound (I). The chains are linked by O—H···O hydrogen bonds involving the lattice water molecules (O3*W* and O4*W*), forming layers parallel to the *bc* plane, as illustrated in Fig. 5 for compound (I). The lattice water molecules are hydrogen bonded to themselves, forming chains that enclose two different $R_4^2(8)$ ring motifs (Fig. 5). Pairs of C—H···O

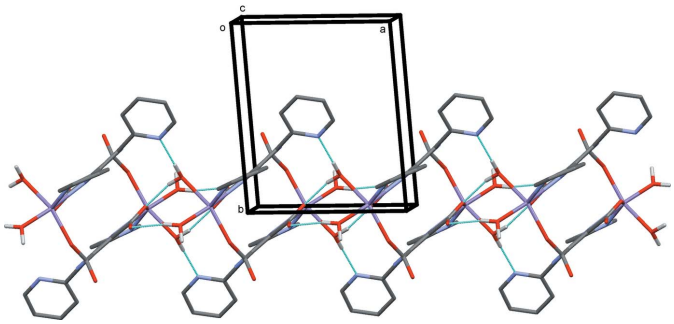


Figure 4
A view along the *c* axis of the chain of complexes propagating along the *a* axis direction. The hydrogen bonds are shown as dashed lines (see Table 3).

hydrogen bonds and offset π–π interactions, involving inversion-related coordinated pyridine rings [$Cg\cdots Cg^{ii}$ = 3.671 (4) Å in (I), and 3.594 (2) Å in (II); *Cg* is the centroid of the ring N3/C5–C9; symmetry code: (ii) $-x+2, -y+2, -z+1$], link the layers, forming a three-dimensional framework; illustrated in Fig. 6 for compound (II).

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.37, last update May 2016; Groom *et al.*, 2016) for the ligand **H$_2$L**, and its dimethyl ester, gave eight hits. Some of these structures have been mentioned in the *Chemical context* above. In the case of (I) and (II), the ligand coordinates to the metal atom in a tridentate (*N,N,O*) and monodentate (*O*) manner. This coordination mode of **H$_2$L** is the same as that observed in the Cd^{II} two-dimensional coordination polymer

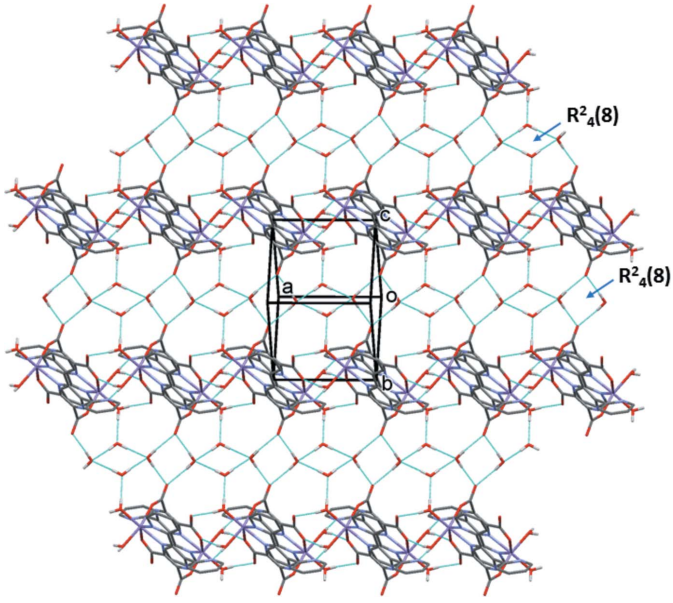


Figure 5
A view along the normal to the *bc* plane of the crystal packing of compound (I). The hydrogen bonds are shown as dashed lines (see Table 3), and the C-bound H atoms have been omitted for clarity.

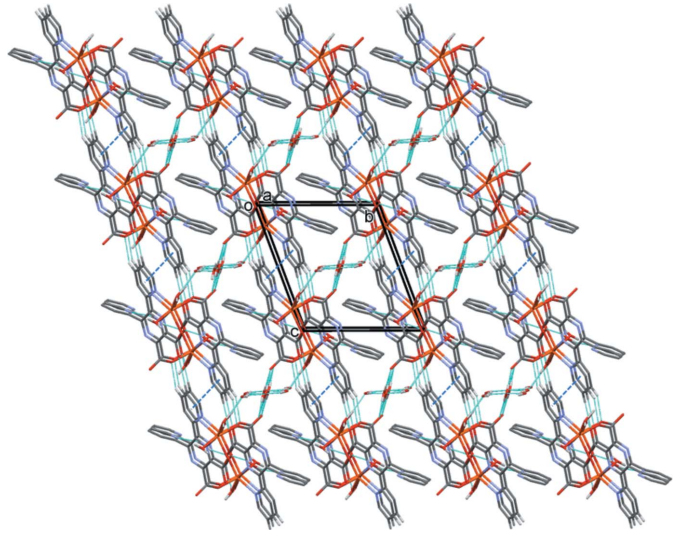


Figure 6
A view along the *a* axis of the crystal packing of compound (II), showing the hydrogen bonds as dashed lines (see Table 4). The offset π–π interactions are shown as dark-blue dashed lines and for clarity only the C-bound H atoms, H7 and H8, have been included.

(Alfonso & Stoeckli-Evans, 2016). The pyridine rings and the carboxylate groups are orientated with respect to the pyrazine ring in a very similar manner for all three compounds.

5. Synthesis and crystallization

The synthesis of the ligand 5,6-bis(pyridin-2-yl)pyrazine-2,3-dicarboxylic acid (**H$_2$L**) has been reported previously (Alfonso *et al.*, 2001).

Synthesis of compound (I): **H$_2$L** (64 mg, 0.20 mmol) was added in solid form to an aqueous solution (15 ml) of $MnCl_2\cdot 4H_2O$ (45 mg, 0.20 mmol). The yellow solution immediately obtained was stirred for 10 min at room temperature, filtered and the filtrate allowed to slowly evaporate. After two weeks orange–yellow rod-like crystals were obtained. They were separated by filtration and dried in air (yield: 54 mg, 54.5%). Selected IR bands (KBr pellet, cm^{-1}): ν 3226(*br*, *s*), 3080(*w*), 1636(*s*), 1598(*vs*), 1545(*w*), 1475(*m*), 1440(*m*), 1410(*w*), 1366(*s*), 1348(*s*), 1301(*w*), 1275(*w*), 1170(*m*), 1126(*m*), 1007(*w*), 954(*w*), 850(*w*), 790(*m*), 562(*m*).

Synthesis of compound (II): A degassed aqueous solution (20 ml) of **H$_2$L** (32 mg, 0.10 mmol) was treated with $FeCl_2\cdot 4H_2O$ (20 mg, 0.10 mmol). The violet solution immediately obtained was stirred under N_2 at 343 K for 1 h, filtered and the filtrate allowed to slowly evaporate. After two months deep-violet block-like crystals were obtained. They were separated by filtration and air dried (yield: 20 mg, 44.6%). Precipitation of small amounts of iron(III) hydroxide accompanied the formation of the crystals. Selected IR bands (KBr pellet, cm^{-1}): ν 3477(*br*, *s*), 3291(*br*, *s*), 3078(*w*), 1640(*s*), 1593(*vs*), 1545(*w*), 1475(*m*), 1440(*m*), 1405(*w*), 1359(*m*), 1300(*w*), 1286(*w*), 1269(*w*), 1172(*m*), 1124(*m*), 1008(*w*), 954(*w*), 847(*w*), 789(*m*), 772(*w*), 677(*w*), 565(*m*), 549(*w*), 494(*m*) %.

Table 5
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[Mn_2(C_{16}H_8N_4O_4)_2(H_2O)_4]\cdot 4H_2O$	$[Fe_2(C_{16}H_8N_4O_4)_2(H_2O)_4]\cdot 4H_2O$
M_r	894.53	896.35
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	293	223
a, b, c (Å)	8.148 (7), 10.4408 (13), 11.5796 (11)	8.0933 (9), 10.3403 (11), 11.5679 (12)
α, β, γ (°)	70.527 (8), 84.232 (9), 84.849 (8)	69.500 (12), 83.593 (13), 84.238 (13)
V (Å^3)	922.4 (8)	899.16 (18)
Z	1	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.77	0.90
Crystal size (mm)	0.38 × 0.27 × 0.23	0.30 × 0.20 × 0.10
Data collection		
Diffractometer	Stoe–Siemens AED2, 4-circle	Stoe IPDS 1 image plate
Absorption correction	–	Multi-scan (*MULABS*; Spek, 2009)
T_{min}, T_{max}	–	0.805, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3244, 3244, 2689	6988, 3202, 2475
R_{int}	0.000	0.063
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.611
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.108, 1.11	0.046, 0.116, 0.97
No. of reflections	3244	3202
No. of parameters	294	294
No. of restraints	8	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.40	0.59, −0.69

Computer programs: *STADI4 Software* (Stoe & Cie, 1997), *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004), *X-RED* Software (Stoe & Cie, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. For both (I) and (II), the water H atoms were located in difference Fourier maps and refined with distance restraints: O—H = 0.84 (2) Å. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.93 Å for (I) and 0.94 Å for (II), with U_{iso}(H) = 1.2U_{eq}(C). Intensity data for (I) were collected at 293 K on a four-circle diffractometer. Only one equivalent of data was measured, hence R_{int} = 0, and as no suitable ψ-scans could be measured no absorption correction was applied. For compound (II), the data were collected at 223 K using a one-circle image-plate diffractometer with which it is not possible to measure 100% of the Ewald sphere, particularly for the triclinic system, hence a small cusp of data was inaccessible.

Acknowledgements

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supporting information

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Isotypic Mn^{II} and Fe^{II} binuclear complexes of the ligand 5,6-bis(pyridin-2-yl)-pyrazine-2,3-dicarboxylic acid

Monserrat Alfonso and Helen Stoeckli-Evans

Computing details

Data collection: *STADI4 Software* (Stoe & Cie, 1997) for (I); *EXPOSE* in *IPDS*-I (Stoe & Cie, 2004) for (II). Cell refinement: *STADI4 Software* (Stoe & Cie, 1997) for (I); *CELL* in *IPDS*-I (Stoe & Cie, 2004) for (II). Data reduction: *X-RED* Software (Stoe & Cie, 1997) for (I); *INTEGRATE* in *IPDS*-I (Stoe & Cie, 2004) for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

(I) Bis[μ-5,6-bis(pyridin-2-yl)pyrazine-2,3-dicarboxylato]-$\kappa^4N^1,O^2,N^6:O^3;\kappa^4O^3:N^1,O^2,N^6$-bis[diaquamanganese(II)] tetrahydrate

Crystal data

$[Mn_2(C_{16}H_8N_4O_4)_2(H_2O)_4]\cdot 4H_2O$
$M_r = 894.53$
Triclinic, $P\overline{1}$
$a = 8.148$ (7) Å
$b = 10.4408$ (13) Å
$c = 11.5796$ (11) Å
$\alpha = 70.527$ (8)°
$\beta = 84.232$ (9)°
$\gamma = 84.849$ (8)°
$V = 922.4$ (8) Å^3
$Z = 1$
$F(000) = 458$
$D_x = 1.610$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 14.0$–$19.7°$
$\mu = 0.77$ mm^{-1}
$T = 293$ K
Block, yellow
0.38 × 0.27 × 0.23 mm

Data collection

Stoe-Siemens AED2, 4-circle diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
ω/\2q scans
3244 measured reflections
3244 independent reflections
2689 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
$h = -9\rightarrow 9$
$k = -11\rightarrow 12$
$l = 0\rightarrow 13$
3 standard reflections every 60 min
intensity decay: 2%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 1.11$
3244 reflections
294 parameters
8 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 1.0007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.70864 (6)	0.99063 (5)	0.82620 (4)	0.02391 (16)
N1	0.9248 (3)	0.8600 (3)	0.9156 (2)	0.0206 (6)
N2	1.1681 (3)	0.6867 (3)	1.0396 (2)	0.0235 (6)
N3	0.8377 (4)	0.8748 (3)	0.7001 (3)	0.0312 (7)
N4	1.4257 (3)	0.6290 (3)	0.8621 (3)	0.0321 (7)
O1	0.7117 (3)	1.0051 (2)	1.0136 (2)	0.0265 (5)
O2	0.8025 (3)	0.9040 (3)	1.2007 (2)	0.0319 (6)
O3	1.1805 (3)	0.8180 (2)	1.2502 (2)	0.0304 (5)
O4	1.0455 (3)	0.6281 (3)	1.3049 (2)	0.0365 (6)
O1W	0.5391 (3)	0.8379 (3)	0.9213 (3)	0.0357 (6)
H1WA	0.455 (4)	0.875 (4)	0.946 (4)	0.051 (13)*
H1WB	0.505 (5)	0.774 (3)	0.903 (4)	0.053 (14)*
O2W	0.5185 (3)	1.0850 (3)	0.7038 (3)	0.0424 (7)
H2WA	0.419 (3)	1.079 (5)	0.733 (4)	0.058 (15)*
H2WB	0.523 (5)	1.166 (2)	0.659 (4)	0.052 (14)*
C1	0.9384 (4)	0.8447 (3)	1.0332 (3)	0.0199 (6)
C2	1.0656 (4)	0.7588 (3)	1.0956 (3)	0.0209 (7)
C3	1.1502 (4)	0.6992 (3)	0.9223 (3)	0.0215 (7)
C4	1.0271 (4)	0.7907 (3)	0.8571 (3)	0.0221 (7)
C5	0.9896 (4)	0.8167 (3)	0.7265 (3)	0.0251 (7)
C6	1.0980 (5)	0.7841 (4)	0.6389 (3)	0.0352 (9)
H6	1.2053	0.7500	0.6567	0.042*
C7	1.0440 (6)	0.8031 (4)	0.5245 (3)	0.0446 (10)
H7	1.1148	0.7812	0.4647	0.053*
C8	0.8856 (6)	0.8542 (4)	0.4996 (3)	0.0466 (11)
H8	0.8455	0.8634	0.4247	0.056*
C9	0.7872 (5)	0.8917 (4)	0.5885 (3)	0.0423 (10)
H9	0.6815	0.9303	0.5706	0.051*
C10	1.2647 (4)	0.6068 (3)	0.8723 (3)	0.0220 (7)
C11	1.2058 (4)	0.5036 (3)	0.8415 (3)	0.0315 (8)
H11	1.0930	0.4917	0.8485	0.038*
C12	1.3179 (5)	0.4179 (4)	0.7999 (3)	0.0359 (9)

H12	1.2817	0.3471	0.7790	0.043*
C13	1.4837 (5)	0.4392 (4)	0.7900 (3)	0.0382 (9)
H13	1.5615	0.3834	0.7621	0.046*
C14	1.5315 (5)	0.5442 (4)	0.8220 (4)	0.0398 (9)
H14	1.6438	0.5576	0.8156	0.048*
C15	0.8067 (4)	0.9252 (3)	1.0883 (3)	0.0220 (7)
C16	1.0965 (4)	0.7345 (3)	1.2291 (3)	0.0249 (7)
O3W	0.5321 (5)	0.3184 (4)	0.5099 (3)	0.0592 (9)
H3WA	0.441 (4)	0.361 (4)	0.496 (4)	0.063 (16)*
H3WB	0.605 (5)	0.376 (4)	0.496 (5)	0.064 (17)*
O4W	0.2287 (4)	0.4854 (4)	0.5048 (3)	0.0541 (8)
H4WA	0.156 (5)	0.450 (5)	0.561 (4)	0.09 (2)*
H4WB	0.177 (6)	0.528 (5)	0.443 (4)	0.09 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0229 (3)	0.0281 (3)	0.0212 (3)	0.0047 (2)	−0.00536 (19)	−0.0092 (2)
N1	0.0206 (13)	0.0254 (14)	0.0170 (13)	0.0020 (11)	−0.0013 (10)	−0.0094 (11)
N2	0.0227 (14)	0.0255 (14)	0.0241 (14)	0.0032 (11)	−0.0052 (11)	−0.0108 (12)
N3	0.0327 (16)	0.0421 (18)	0.0229 (15)	0.0071 (13)	−0.0094 (12)	−0.0164 (13)
N4	0.0252 (15)	0.0384 (17)	0.0387 (17)	0.0029 (13)	−0.0029 (13)	−0.0216 (14)
O1	0.0291 (12)	0.0296 (12)	0.0214 (12)	0.0084 (10)	−0.0043 (10)	−0.0110 (10)
O2	0.0309 (13)	0.0458 (15)	0.0210 (12)	0.0088 (11)	−0.0020 (10)	−0.0164 (11)
O3	0.0360 (14)	0.0363 (14)	0.0222 (12)	−0.0046 (11)	−0.0076 (10)	−0.0117 (10)
O4	0.0466 (16)	0.0360 (15)	0.0234 (13)	−0.0105 (12)	−0.0068 (11)	−0.0020 (11)
O1W	0.0290 (14)	0.0340 (15)	0.0490 (17)	−0.0058 (12)	0.0061 (12)	−0.0218 (13)
O2W	0.0254 (15)	0.0521 (19)	0.0360 (16)	0.0046 (13)	−0.0067 (12)	0.0031 (14)
C1	0.0225 (16)	0.0194 (16)	0.0172 (15)	−0.0022 (13)	0.0000 (12)	−0.0054 (12)
C2	0.0200 (16)	0.0236 (16)	0.0206 (16)	−0.0034 (13)	−0.0028 (13)	−0.0083 (13)
C3	0.0216 (16)	0.0218 (16)	0.0220 (16)	−0.0013 (13)	−0.0027 (13)	−0.0082 (13)
C4	0.0243 (17)	0.0245 (17)	0.0190 (16)	0.0026 (13)	−0.0032 (13)	−0.0096 (13)
C5	0.0330 (19)	0.0270 (17)	0.0169 (16)	0.0049 (14)	−0.0045 (14)	−0.0101 (14)
C6	0.040 (2)	0.041 (2)	0.0242 (18)	0.0142 (17)	−0.0039 (15)	−0.0133 (16)
C7	0.071 (3)	0.044 (2)	0.0187 (18)	0.012 (2)	0.0017 (18)	−0.0150 (17)
C8	0.071 (3)	0.051 (3)	0.0219 (19)	0.011 (2)	−0.0142 (19)	−0.0184 (18)
C9	0.046 (2)	0.054 (3)	0.031 (2)	0.0112 (19)	−0.0190 (18)	−0.0183 (19)
C10	0.0229 (16)	0.0230 (16)	0.0201 (16)	0.0048 (13)	−0.0050 (13)	−0.0078 (13)
C11	0.0291 (18)	0.0278 (19)	0.038 (2)	−0.0011 (15)	−0.0004 (15)	−0.0122 (16)
C12	0.049 (2)	0.0256 (19)	0.036 (2)	0.0006 (17)	−0.0038 (17)	−0.0142 (16)
C13	0.041 (2)	0.039 (2)	0.038 (2)	0.0157 (17)	−0.0044 (17)	−0.0209 (18)
C14	0.0249 (19)	0.051 (2)	0.051 (2)	0.0086 (17)	−0.0060 (17)	−0.029 (2)
C15	0.0206 (16)	0.0254 (17)	0.0229 (17)	−0.0040 (13)	−0.0004 (13)	−0.0113 (14)
C16	0.0221 (17)	0.0307 (19)	0.0223 (17)	0.0063 (14)	−0.0058 (13)	−0.0100 (15)
O3W	0.052 (2)	0.050 (2)	0.062 (2)	0.0047 (18)	−0.0119 (17)	0.0001 (16)
O4W	0.0378 (17)	0.066 (2)	0.0458 (19)	0.0026 (15)	−0.0105 (15)	0.0000 (16)

Geometric parameters (Å, º)

Mn1—O3^{i}	2.139 (2)	C2—C16	1.524 (4)
Mn1—O1W	2.141 (3)	C3—C4	1.410 (4)
Mn1—O2W	2.148 (3)	C3—C10	1.496 (4)
Mn1—O1	2.228 (2)	C4—C5	1.502 (4)
Mn1—N1	2.242 (3)	C5—C6	1.386 (5)
Mn1—N3	2.311 (3)	C6—C7	1.383 (5)
N1—C1	1.333 (4)	C6—H6	0.9300
N1—C4	1.335 (4)	C7—C8	1.372 (6)
N2—C2	1.337 (4)	C7—H7	0.9300
N2—C3	1.342 (4)	C8—C9	1.379 (6)
N3—C9	1.345 (4)	C8—H8	0.9300
N3—C5	1.346 (4)	C9—H9	0.9300
N4—C10	1.339 (4)	C10—C11	1.380 (5)
N4—C14	1.341 (4)	C11—C12	1.385 (5)
O1—C15	1.257 (4)	C11—H11	0.9300
O2—C15	1.243 (4)	C12—C13	1.376 (5)
O3—C16	1.254 (4)	C12—H12	0.9300
O3—Mn1^{i}	2.139 (2)	C13—C14	1.367 (5)
O4—C16	1.239 (4)	C13—H13	0.9300
O1W—H1WA	0.831 (19)	C14—H14	0.9300
O1W—H1WB	0.839 (19)	O3W—H3WA	0.834 (19)
O2W—H2WA	0.841 (19)	O3W—H3WB	0.851 (19)
O2W—H2WB	0.833 (19)	O4W—H4WA	0.84 (2)
C1—C2	1.397 (4)	O4W—H4WB	0.84 (2)
C1—C15	1.524 (4)		

O3^{i}—Mn1—O1W	162.15 (10)	N1—C4—C5	113.8 (3)
O3^{i}—Mn1—O2W	85.00 (11)	C3—C4—C5	127.3 (3)
O1W—Mn1—O2W	86.92 (12)	N3—C5—C6	121.5 (3)
O3^{i}—Mn1—O1	89.80 (9)	N3—C5—C4	114.0 (3)
O1W—Mn1—O1	81.62 (10)	C6—C5—C4	124.5 (3)
O2W—Mn1—O1	124.11 (10)	C7—C6—C5	118.9 (3)
O3^{i}—Mn1—N1	99.80 (10)	C7—C6—H6	120.5
O1W—Mn1—N1	92.39 (11)	C5—C6—H6	120.5
O2W—Mn1—N1	163.62 (11)	C8—C7—C6	119.7 (3)
O1—Mn1—N1	71.84 (8)	C8—C7—H7	120.1
O3^{i}—Mn1—N3	100.80 (10)	C6—C7—H7	120.1
O1W—Mn1—N3	95.57 (11)	C7—C8—C9	118.3 (3)
O2W—Mn1—N3	93.71 (11)	C7—C8—H8	120.8
O1—Mn1—N3	141.63 (9)	C9—C8—H8	120.8
N1—Mn1—N3	70.05 (9)	N3—C9—C8	122.8 (4)
C1—N1—C4	121.1 (3)	N3—C9—H9	118.6
C1—N1—Mn1	117.1 (2)	C8—C9—H9	118.6
C4—N1—Mn1	121.5 (2)	N4—C10—C11	122.8 (3)
C2—N2—C3	119.7 (3)	N4—C10—C3	116.1 (3)
C9—N3—C5	118.5 (3)	C11—C10—C3	121.1 (3)

C9—N3—Mn1	122.3 (2)	C10—C11—C12	118.7 (3)
C5—N3—Mn1	117.1 (2)	C10—C11—H11	120.7
C10—N4—C14	117.2 (3)	C12—C11—H11	120.7
C15—O1—Mn1	119.75 (19)	C13—C12—C11	119.0 (3)
C16—O3—Mn1^{i}	145.3 (2)	C13—C12—H12	120.5
Mn1—O1W—H1WA	108 (3)	C11—C12—H12	120.5
Mn1—O1W—H1WB	132 (3)	C14—C13—C12	118.6 (3)
H1WA—O1W—H1WB	105 (4)	C14—C13—H13	120.7
Mn1—O2W—H2WA	118 (3)	C12—C13—H13	120.7
Mn1—O2W—H2WB	121 (3)	N4—C14—C13	123.7 (4)
H2WA—O2W—H2WB	104 (4)	N4—C14—H14	118.1
N1—C1—C2	119.7 (3)	C13—C14—H14	118.1
N1—C1—C15	114.6 (3)	O2—C15—O1	127.1 (3)
C2—C1—C15	125.7 (3)	O2—C15—C1	117.5 (3)
N2—C2—C1	120.2 (3)	O1—C15—C1	115.4 (3)
N2—C2—C16	114.9 (3)	O4—C16—O3	126.5 (3)
C1—C2—C16	124.9 (3)	O4—C16—C2	116.0 (3)
N2—C3—C4	120.3 (3)	O3—C16—C2	117.2 (3)
N2—C3—C10	114.7 (3)	H3WA—O3W—H3WB	108 (5)
C4—C3—C10	124.9 (3)	H4WA—O4W—H4WB	106 (5)
N1—C4—C3	118.8 (3)		

C4—N1—C1—C2	2.5 (5)	C5—C6—C7—C8	0.4 (6)
Mn1—N1—C1—C2	176.7 (2)	C6—C7—C8—C9	3.2 (6)
C4—N1—C1—C15	−176.9 (3)	C5—N3—C9—C8	−1.1 (6)
Mn1—N1—C1—C15	−2.7 (3)	Mn1—N3—C9—C8	161.9 (3)
C3—N2—C2—C1	1.2 (5)	C7—C8—C9—N3	−2.9 (7)
C3—N2—C2—C16	179.1 (3)	C14—N4—C10—C11	−1.2 (5)
N1—C1—C2—N2	−3.5 (5)	C14—N4—C10—C3	177.5 (3)
C15—C1—C2—N2	175.8 (3)	N2—C3—C10—N4	−65.6 (4)
N1—C1—C2—C16	178.9 (3)	C4—C3—C10—N4	116.5 (4)
C15—C1—C2—C16	−1.8 (5)	N2—C3—C10—C11	113.1 (3)
C2—N2—C3—C4	1.9 (5)	C4—C3—C10—C11	−64.8 (5)
C2—N2—C3—C10	−176.2 (3)	N4—C10—C11—C12	1.0 (5)
C1—N1—C4—C3	0.6 (5)	C3—C10—C11—C12	−177.6 (3)
Mn1—N1—C4—C3	−173.3 (2)	C10—C11—C12—C13	−0.4 (5)
C1—N1—C4—C5	177.8 (3)	C11—C12—C13—C14	0.2 (6)
Mn1—N1—C4—C5	3.9 (4)	C10—N4—C14—C13	0.9 (6)
N2—C3—C4—N1	−2.8 (5)	C12—C13—C14—N4	−0.4 (6)
C10—C3—C4—N1	175.0 (3)	Mn1—O1—C15—O2	−166.2 (3)
N2—C3—C4—C5	−179.7 (3)	Mn1—O1—C15—C1	12.6 (4)
C10—C3—C4—C5	−1.8 (5)	N1—C1—C15—O2	172.6 (3)
C9—N3—C5—C6	4.9 (5)	C2—C1—C15—O2	−6.7 (5)
Mn1—N3—C5—C6	−158.9 (3)	N1—C1—C15—O1	−6.3 (4)
C9—N3—C5—C4	−174.5 (3)	C2—C1—C15—O1	174.3 (3)
Mn1—N3—C5—C4	21.7 (4)	Mn1^{i}—O3—C16—O4	−176.0 (3)
N1—C4—C5—N3	−16.8 (4)	Mn1^{i}—O3—C16—C2	9.6 (5)
C3—C4—C5—N3	160.2 (3)	N2—C2—C16—O4	−77.6 (4)

N1—C4—C5—C6	163.8 (3)	C1—C2—C16—O4	100.2 (4)
C3—C4—C5—C6	−19.2 (6)	N2—C2—C16—O3	97.5 (4)
N3—C5—C6—C7	−4.6 (6)	C1—C2—C16—O3	−84.8 (4)
C4—C5—C6—C7	174.8 (3)		

Symmetry code: (i) −*x*+2, −*y*+2, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1^{ii}	0.83 (2)	1.89 (2)	2.710 (4)	168 (4)
O1*W*—H1*WB*···N4^{iii}	0.84 (2)	1.91 (2)	2.750 (4)	179 (5)
O2*W*—H2*WA*···O2^{ii}	0.84 (2)	1.91 (2)	2.743 (4)	170 (5)
O2*W*—H2*WB*···O3*W*^{iv}	0.83 (2)	1.92 (3)	2.710 (4)	159 (4)
O3*W*—H3*WA*···O4*W*	0.83 (2)	2.08 (2)	2.888 (5)	163 (5)
O3*W*—H3*WB*···O4*W*^{v}	0.85 (2)	2.07 (2)	2.906 (5)	169 (5)
O4*W*—H4*WA*···O4^{vi}	0.84 (2)	2.16 (2)	3.000 (4)	175 (6)
O4*W*—H4*WB*···O4^{vii}	0.84 (2)	1.95 (2)	2.793 (4)	176 (6)
C7—H7···O3^{viii}	0.93	2.40	3.216 (5)	147
C8—H8···O2^{viii}	0.93	2.54	3.452 (4)	167

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+2; (iii) *x*−1, *y*, *z*; (iv) *x*, *y*+1, *z*; (v) −*x*+1, −*y*+1, −*z*+1; (vi) −*x*+1, −*y*+1, −*z*+2; (vii) *x*−1, *y*, *z*−1; (viii) *x*, *y*, *z*−1.

(II) Bis[*μ*-5,6-bis(pyridin-2-yl)pyrazine-2,3-dicarboxylato]-$\kappa^4N^1,O^2,N^6:O^3;\kappa^4O^3:N^1,O^2,N^6$-bis[diaquairon(II)] tetrahydrate

Crystal data

$[Fe_2(C_{16}H_8N_4O_4)_2(H_2O)_4]\cdot 4H_2O$
M_r = 896.35
Triclinic, $P\overline{1}$
a = 8.0933 (9) Å
b = 10.3403 (11) Å
c = 11.5679 (12) Å
α = 69.500 (12)°
β = 83.593 (13)°
γ = 84.238 (13)°
V = 899.16 (18) Å^3
Z = 1
F(000) = 460
D_x = 1.655 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5000 reflections
θ = 3.3–52.1°
μ = 0.90 mm^{-1}
T = 223 K
Block, dark-violet
0.30 × 0.20 × 0.10 mm

Data collection

Stoe IPDS 1 image plate diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
φ rotation scans
Absorption correction: multi-scan (MULABS; Spek, 2009)
T_{min} = 0.805, T_{max} = 1.000
6988 measured reflections
3202 independent reflections
2475 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 25.7°, θ_{min} = 2.1°
h = −9→9
k = −12→12
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.116$
$S = 0.97$
3202 reflections
294 parameters
8 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.072P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.71296 (5)	0.99041 (4)	0.82831 (4)	0.01544 (16)
N1	0.9194 (3)	0.8624 (2)	0.9131 (2)	0.0142 (5)
N2	1.1679 (3)	0.6879 (2)	1.0372 (2)	0.0154 (6)
N3	0.8286 (3)	0.8855 (3)	0.7002 (3)	0.0202 (6)
N4	1.4267 (3)	0.6299 (3)	0.8589 (3)	0.0226 (6)
O1	0.7040 (3)	1.00868 (19)	1.0068 (2)	0.0165 (5)
O2	0.7957 (3)	0.9106 (2)	1.1961 (2)	0.0211 (5)
O3	1.1738 (3)	0.8201 (2)	1.2494 (2)	0.0194 (5)
O4	1.0447 (3)	0.6252 (2)	1.3039 (2)	0.0245 (5)
O1W	0.5488 (3)	0.8329 (2)	0.9222 (2)	0.0225 (5)
H1WA	0.463 (3)	0.863 (4)	0.955 (4)	0.040 (12)*
H1WB	0.508 (6)	0.784 (5)	0.891 (5)	0.078 (18)*
O2W	0.5259 (3)	1.0878 (2)	0.7138 (3)	0.0277 (6)
H2WA	0.423 (3)	1.080 (4)	0.744 (3)	0.028 (10)*
H2WB	0.547 (5)	1.160 (3)	0.654 (3)	0.030 (11)*
C1	0.9344 (3)	0.8476 (3)	1.0307 (3)	0.0123 (6)
C2	1.0637 (4)	0.7604 (3)	1.0931 (3)	0.0137 (6)
C3	1.1487 (4)	0.7011 (3)	0.9199 (3)	0.0151 (7)
C4	1.0221 (4)	0.7921 (3)	0.8542 (3)	0.0139 (6)
C5	0.9805 (4)	0.8186 (3)	0.7251 (3)	0.0182 (7)
C6	1.0827 (4)	0.7811 (3)	0.6371 (3)	0.0254 (8)
H6	1.1908	0.7411	0.6540	0.031*
C7	1.0240 (5)	0.8032 (3)	0.5224 (4)	0.0320 (9)
H7	1.0915	0.7775	0.4614	0.038*
C8	0.8663 (5)	0.8629 (4)	0.4998 (4)	0.0326 (9)
H8	0.8218	0.8744	0.4249	0.039*
C9	0.7745 (5)	0.9057 (3)	0.5888 (3)	0.0292 (8)
H9	0.6690	0.9512	0.5710	0.035*

C10	1.2661 (4)	0.6075 (3)	0.8702 (3)	0.0150 (6)
C11	1.2068 (4)	0.5027 (3)	0.8409 (3)	0.0212 (7)
H11	1.0922	0.4899	0.8496	0.025*
C12	1.3217 (4)	0.4167 (3)	0.7982 (3)	0.0252 (8)
H12	1.2857	0.3450	0.7768	0.030*
C13	1.4882 (4)	0.4381 (3)	0.7877 (3)	0.0268 (8)
H13	1.5685	0.3808	0.7601	0.032*
C14	1.5346 (4)	0.5459 (3)	0.8187 (4)	0.0282 (8)
H14	1.6486	0.5608	0.8111	0.034*
C15	0.8008 (3)	0.9290 (3)	1.0849 (3)	0.0137 (6)
C16	1.0942 (4)	0.7348 (3)	1.2273 (3)	0.0162 (7)
O3W	0.5377 (4)	0.3176 (3)	0.5121 (3)	0.0389 (7)
H3WA	0.448 (4)	0.365 (5)	0.507 (6)	0.08 (2)*
H3WB	0.611 (4)	0.374 (4)	0.500 (4)	0.044 (13)*
O4W	0.2296 (3)	0.4837 (3)	0.5051 (3)	0.0351 (6)
H4WA	0.159 (5)	0.448 (4)	0.564 (3)	0.050 (14)*
H4WB	0.177 (7)	0.527 (6)	0.445 (4)	0.10 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0188 (3)	0.0121 (2)	0.0149 (3)	0.00398 (16)	−0.00588 (18)	−0.00385 (17)
N1	0.0159 (12)	0.0098 (11)	0.0163 (16)	0.0009 (9)	−0.0017 (11)	−0.0042 (10)
N2	0.0175 (13)	0.0114 (11)	0.0181 (16)	0.0014 (9)	−0.0042 (11)	−0.0058 (11)
N3	0.0237 (14)	0.0199 (13)	0.0170 (17)	0.0032 (11)	−0.0073 (12)	−0.0059 (12)
N4	0.0202 (14)	0.0204 (13)	0.0297 (19)	0.0033 (11)	−0.0044 (13)	−0.0124 (12)
O1	0.0200 (11)	0.0132 (9)	0.0166 (13)	0.0053 (8)	−0.0049 (9)	−0.0062 (9)
O2	0.0211 (11)	0.0273 (11)	0.0154 (14)	0.0050 (9)	−0.0034 (10)	−0.0093 (10)
O3	0.0269 (12)	0.0160 (10)	0.0155 (13)	−0.0035 (9)	−0.0053 (10)	−0.0042 (9)
O4	0.0328 (13)	0.0183 (11)	0.0173 (14)	−0.0067 (9)	−0.0059 (11)	0.0028 (10)
O1W	0.0193 (12)	0.0168 (11)	0.0338 (16)	−0.0020 (9)	0.0023 (11)	−0.0128 (11)
O2W	0.0184 (13)	0.0250 (12)	0.0284 (17)	0.0022 (10)	−0.0067 (11)	0.0052 (11)
C1	0.0154 (14)	0.0083 (12)	0.0130 (18)	−0.0002 (11)	−0.0014 (13)	−0.0035 (12)
C2	0.0173 (15)	0.0090 (12)	0.0143 (18)	−0.0028 (11)	−0.0015 (13)	−0.0027 (12)
C3	0.0161 (15)	0.0096 (13)	0.020 (2)	−0.0005 (11)	−0.0012 (13)	−0.0055 (12)
C4	0.0168 (15)	0.0111 (13)	0.0147 (18)	−0.0010 (11)	−0.0004 (13)	−0.0058 (12)
C5	0.0247 (16)	0.0110 (13)	0.018 (2)	0.0022 (12)	−0.0030 (14)	−0.0048 (13)
C6	0.0363 (19)	0.0189 (15)	0.020 (2)	0.0123 (14)	−0.0055 (16)	−0.0077 (14)
C7	0.052 (2)	0.0223 (16)	0.019 (2)	0.0090 (16)	−0.0002 (18)	−0.0073 (15)
C8	0.053 (2)	0.0293 (18)	0.018 (2)	0.0063 (16)	−0.0142 (18)	−0.0112 (16)
C9	0.037 (2)	0.0278 (17)	0.024 (2)	0.0082 (15)	−0.0119 (17)	−0.0110 (16)
C10	0.0209 (15)	0.0111 (13)	0.0108 (18)	0.0028 (11)	−0.0054 (13)	−0.0007 (12)
C11	0.0232 (16)	0.0131 (14)	0.027 (2)	0.0000 (12)	−0.0036 (15)	−0.0058 (14)
C12	0.0371 (19)	0.0139 (14)	0.025 (2)	0.0012 (13)	−0.0041 (16)	−0.0069 (14)
C13	0.0325 (19)	0.0201 (15)	0.027 (2)	0.0112 (14)	−0.0035 (16)	−0.0102 (15)
C14	0.0190 (17)	0.0296 (17)	0.038 (3)	0.0072 (13)	−0.0039 (16)	−0.0166 (17)
C15	0.0140 (14)	0.0110 (13)	0.018 (2)	−0.0007 (11)	−0.0031 (13)	−0.0067 (12)
C16	0.0159 (15)	0.0153 (14)	0.0166 (19)	0.0044 (12)	−0.0041 (13)	−0.0050 (13)

O3W	0.0379 (17)	0.0250 (13)	0.042 (2)	0.0034 (12)	−0.0074 (14)	0.0028 (12)
O4W	0.0258 (14)	0.0379 (15)	0.0308 (19)	−0.0003 (11)	−0.0060 (13)	0.0024 (13)

Geometric parameters (Å, º)

Fe1—O3^{i}	2.105 (2)	C2—C16	1.525 (4)
Fe1—O1W	2.115 (2)	C3—C4	1.411 (4)
Fe1—O2W	2.066 (2)	C3—C10	1.502 (4)
Fe1—O1	2.131 (2)	C4—C5	1.492 (4)
Fe1—N1	2.126 (2)	C5—C6	1.377 (5)
Fe1—N3	2.205 (3)	C6—C7	1.394 (5)
N1—C1	1.333 (4)	C6—H6	0.9400
N1—C4	1.335 (4)	C7—C8	1.372 (5)
N2—C2	1.335 (4)	C7—H7	0.9400
N2—C3	1.340 (4)	C8—C9	1.374 (5)
N3—C9	1.347 (4)	C8—H8	0.9400
N3—C5	1.357 (4)	C9—H9	0.9400
N4—C10	1.327 (4)	C10—C11	1.385 (4)
N4—C14	1.331 (4)	C11—C12	1.391 (5)
O1—C15	1.271 (4)	C11—H11	0.9400
O2—C15	1.229 (4)	C12—C13	1.373 (5)
O3—C16	1.251 (3)	C12—H12	0.9400
O3—Fe1^{i}	2.105 (2)	C13—C14	1.381 (5)
O4—C16	1.240 (4)	C13—H13	0.9400
O1W—H1WA	0.836 (19)	C14—H14	0.9400
O1W—H1WB	0.83 (2)	O3W—H3WA	0.83 (2)
O2W—H2WA	0.867 (19)	O3W—H3WB	0.843 (19)
O2W—H2WB	0.840 (19)	O4W—H4WA	0.842 (19)
C1—C2	1.398 (4)	O4W—H4WB	0.82 (2)
C1—C15	1.519 (4)		
O3^{i}—Fe1—O1W	164.77 (9)	N1—C4—C5	113.3 (2)
O3^{i}—Fe1—O2W	85.22 (9)	C3—C4—C5	128.5 (3)
O1W—Fe1—O2W	87.43 (10)	N3—C5—C6	121.7 (3)
O3^{i}—Fe1—O1	89.65 (8)	N3—C5—C4	113.3 (3)
O1W—Fe1—O1	82.38 (9)	C6—C5—C4	125.0 (3)
O2W—Fe1—O1	119.49 (10)	C5—C6—C7	119.2 (3)
O3^{i}—Fe1—N1	99.21 (9)	C5—C6—H6	120.4
O1W—Fe1—N1	91.27 (9)	C7—C6—H6	120.4
O2W—Fe1—N1	165.15 (10)	C8—C7—C6	119.1 (3)
N1—Fe1—O1	74.91 (9)	C8—C7—H7	120.4
O3^{i}—Fe1—N3	99.60 (9)	C6—C7—H7	120.4
O1W—Fe1—N3	94.03 (10)	C7—C8—C9	118.7 (3)
O2W—Fe1—N3	92.45 (10)	C7—C8—H8	120.6
O1—Fe1—N3	147.49 (9)	C9—C8—H8	120.6
N1—Fe1—N3	72.87 (10)	N3—C9—C8	123.1 (3)
C1—N1—C4	121.5 (2)	N3—C9—H9	118.4
C1—N1—Fe1	116.87 (19)	C8—C9—H9	118.4

C4—N1—Fe1	121.4 (2)	N4—C10—C11	123.0 (3)
C2—N2—C3	119.3 (2)	N4—C10—C3	116.3 (2)
C9—N3—C5	117.9 (3)	C11—C10—C3	120.7 (3)
C9—N3—Fe1	124.0 (2)	C10—C11—C12	118.2 (3)
C5—N3—Fe1	116.9 (2)	C10—C11—H11	120.9
C10—N4—C14	117.9 (3)	C12—C11—H11	120.9
C15—O1—Fe1	118.95 (19)	C13—C12—C11	119.1 (3)
C16—O3—Fe1^{i}	144.9 (2)	C13—C12—H12	120.4
Fe1—O1W—H1WA	112 (3)	C11—C12—H12	120.4
Fe1—O1W—H1WB	126 (4)	C12—C13—C14	118.2 (3)
H1WA—O1W—H1WB	101 (4)	C12—C13—H13	120.9
Fe1—O2W—H2WA	119 (3)	C14—C13—H13	120.9
Fe1—O2W—H2WB	118 (3)	N4—C14—C13	123.5 (3)
H2WA—O2W—H2WB	117 (4)	N4—C14—H14	118.2
N1—C1—C2	119.6 (3)	C13—C14—H14	118.2
N1—C1—C15	114.3 (2)	O2—C15—O1	127.5 (3)
C2—C1—C15	126.1 (3)	O2—C15—C1	118.4 (2)
N2—C2—C1	120.4 (3)	O1—C15—C1	114.0 (3)
N2—C2—C16	115.0 (2)	O4—C16—O3	126.2 (3)
C1—C2—C16	124.6 (3)	O4—C16—C2	115.5 (2)
N2—C3—C4	121.1 (3)	O3—C16—C2	118.2 (3)
N2—C3—C10	114.3 (2)	H3WA—O3W—H3WB	105 (4)
C4—C3—C10	124.6 (3)	H4WA—O4W—H4WB	107 (5)
N1—C4—C3	118.1 (3)		

C4—N1—C1—C2	2.2 (4)	C5—C6—C7—C8	0.6 (5)
Fe1—N1—C1—C2	177.48 (19)	C6—C7—C8—C9	3.4 (5)
C4—N1—C1—C15	−176.6 (2)	C5—N3—C9—C8	−0.6 (5)
Fe1—N1—C1—C15	−1.3 (3)	Fe1—N3—C9—C8	166.1 (3)
C3—N2—C2—C1	1.0 (4)	C7—C8—C9—N3	−3.5 (6)
C3—N2—C2—C16	178.6 (2)	C14—N4—C10—C11	−0.8 (5)
N1—C1—C2—N2	−2.7 (4)	C14—N4—C10—C3	177.9 (3)
C15—C1—C2—N2	176.0 (2)	N2—C3—C10—N4	−65.1 (4)
N1—C1—C2—C16	−180.0 (2)	C4—C3—C10—N4	117.8 (3)
C15—C1—C2—C16	−1.4 (4)	N2—C3—C10—C11	113.7 (3)
C2—N2—C3—C4	1.1 (4)	C4—C3—C10—C11	−63.5 (4)
C2—N2—C3—C10	−176.2 (2)	N4—C10—C11—C12	0.3 (5)
C1—N1—C4—C3	−0.2 (4)	C3—C10—C11—C12	−178.3 (3)
Fe1—N1—C4—C3	−175.24 (19)	C10—C11—C12—C13	0.5 (5)
C1—N1—C4—C5	177.6 (2)	C11—C12—C13—C14	−0.8 (5)
Fe1—N1—C4—C5	2.6 (3)	C10—N4—C14—C13	0.4 (5)
N2—C3—C4—N1	−1.5 (4)	C12—C13—C14—N4	0.3 (6)
C10—C3—C4—N1	175.5 (3)	Fe1—O1—C15—O2	−168.1 (2)
N2—C3—C4—C5	−178.9 (3)	Fe1—O1—C15—C1	10.8 (3)
C10—C3—C4—C5	−2.0 (5)	N1—C1—C15—O2	172.9 (2)
C9—N3—C5—C6	4.8 (4)	C2—C1—C15—O2	−5.8 (4)
Fe1—N3—C5—C6	−162.8 (2)	N1—C1—C15—O1	−6.1 (3)
C9—N3—C5—C4	−175.5 (3)	C2—C1—C15—O1	175.2 (3)

Fe1—N3—C5—C4	16.9 (3)	Fe1^{i}—O3—C16—O4	180.0 (2)
N1—C4—C5—N3	−12.7 (4)	Fe1^{i}—O3—C16—C2	4.6 (5)
C3—C4—C5—N3	164.8 (3)	N2—C2—C16—O4	−76.7 (3)
N1—C4—C5—C6	167.0 (3)	C1—C2—C16—O4	100.8 (3)
C3—C4—C5—C6	−15.4 (5)	N2—C2—C16—O3	99.2 (3)
N3—C5—C6—C7	−4.8 (5)	C1—C2—C16—O3	−83.4 (4)
C4—C5—C6—C7	175.5 (3)		

Symmetry code: (i) −*x*+2, −*y*+2, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1^{ii}	0.84 (2)	1.93 (2)	2.728 (3)	160 (4)
O1*W*—H1*WB*···N4^{iii}	0.83 (2)	1.94 (2)	2.752 (3)	165 (6)
O2*W*—H2*WA*···O2^{ii}	0.87 (2)	1.83 (2)	2.694 (3)	172 (3)
O2*W*—H2*WB*···O3*W*^{iv}	0.84 (2)	1.87 (2)	2.686 (4)	165 (4)
O3*W*—H3*WA*···O4*W*	0.83 (2)	2.04 (2)	2.874 (4)	176 (6)
O3*W*—H3*WB*···O4*W*^{v}	0.84 (2)	2.03 (2)	2.866 (4)	171 (4)
O4*W*—H4*WA*···O4^{vi}	0.84 (2)	2.12 (2)	2.957 (4)	172 (5)
O4*W*—H4*WB*···O4^{vii}	0.82 (2)	1.96 (2)	2.784 (4)	178 (7)
C7—H7···O3^{viii}	0.94	2.36	3.206 (5)	149
C8—H8···O2^{viii}	0.94	2.57	3.477 (4)	162

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+2; (iii) *x*−1, *y*, *z*; (iv) *x*, *y*+1, *z*; (v) −*x*+1, −*y*+1, −*z*+1; (vi) −*x*+1, −*y*+1, −*z*+2; (vii) *x*−1, *y*, *z*−1; (viii) *x*, *y*, *z*−1.