

Solvent water tapes in two hydrates of μ -oxo-bis[bis(2,2'-bipyridine- κ^2 N,N')-(sulfato- κ O)iron(III)]

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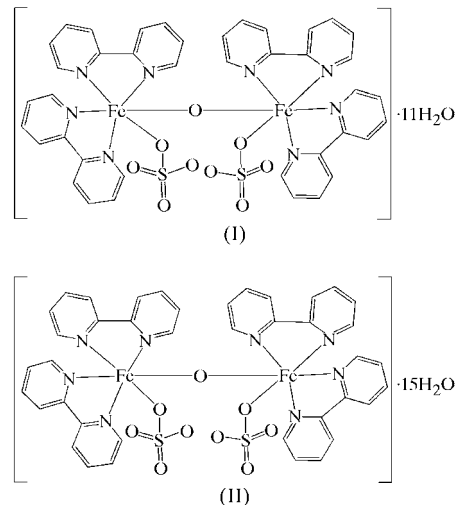
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The title compound, $[\text{Fe}_2\text{O}(\text{SO}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_4]$, crystallizes as two different hydrates, *viz.* $11\text{H}_2\text{O}$, (I), and $15\text{H}_2\text{O}$, (II). The complex is binuclear, in which the two Fe^{III} atoms are coordinated in an octahedral geometry to four N atoms from the two bipyridine ligands, to one O atom from the sulfate ion and to an oxo ion on a twofold axis, which acts as a bridge between the symmetry-related units. The $\text{Fe}\cdots\text{Fe}$ separation is 3.556 (4) Å and the $\text{Fe}-\text{O}-\text{Fe}$ angle is 161.6 (2)° in (I); the corresponding values are 3.544 (1) Å and 165.8 (2)° in (II). In (II), one of the O atoms of the sulfate ion is disordered over two positions. In both compounds, the solvent water molecules form slightly different one-dimensional hydrogen-bonded networks which pass along the *c* axis of the unit cell. In (I), three solvent water molecules and, in (II), one solvent water molecule, are situated on the twofold axis. In both (I) and (II), the central O atom of the metal complex lies on a twofold axis.

Comment

Oxo-bridged dinuclear Fe^{III} complexes are of interest due to their magnetic properties resulting from superexchange *via* the oxo bridge (Wernsdorfer & Sessoli, 1999). Moreover, they have been studied as potential models for several non-haem iron centres in biological systems (Feig & Lippard, 1994). Compounds with a single oxo bridge are less common than those containing additional multi-atom bridges, notably carboxylate bridges (Kurtz, 1990). It has long been known that the treatment of Fe^{III} salts with 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) in an aqueous medium results in dinuclear complexes (Khedekar *et al.*, 1967). Several complexes having the $[\text{Fe}_2\text{O}(\text{phen})_4]^{4+}$ core have been structurally characterized to date. However, the structures of only two bpy complexes of this type (Xiang *et al.*, 1998; Choudhury *et al.*, 1997) and its 4,4-dimethyl-2,2'-bipyridine analogue (Collomb *et al.*, 1999; Menage *et al.*, 1993) have so far been reported. In this paper, we report the structures of two

hydrates of the bpy complex obtained with Fe^{III} sulfate, $[\text{Fe}_2(\mu\text{-O})(\text{SO}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_4]\cdot 11\text{H}_2\text{O}$, (I), and $[\text{Fe}_2(\mu\text{-O})(\text{SO}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_4]\cdot 15\text{H}_2\text{O}$, (II). A previous preparation is said to have yielded a precipitate having 3.5 water molecules per dimer, but this has not been structurally characterized (Reiff *et al.*, 1968).



We obtained hydrates (I) and (II) in an attempt to prepare mixed-ligand complexes. Compound (I) was obtained in a reaction of ferric sulfate with bpy and sodium acetate, while (II) was obtained when 1,2-diaminoethane was used in place of sodium acetate. Both structures consist of a dinuclear molecule in which two symmetry-related Fe^{III} atoms are bridged by an oxo ion situated on a twofold axis (Figs. 1 and 2). Selected bond distances and angles and hydrogen-bond parameters are shown in Tables 1–4.

The coordination around each metal atom, which may be described as *cis*-distorted octahedral, is completed by an O atom from the sulfate ion and two chelating bpy ligands. The $\text{Fe}-\text{N}$ bonds *trans* to the O atoms in the equatorial plane are significantly longer than the axial $\text{Fe}-\text{N}$ bonds. The equatorial

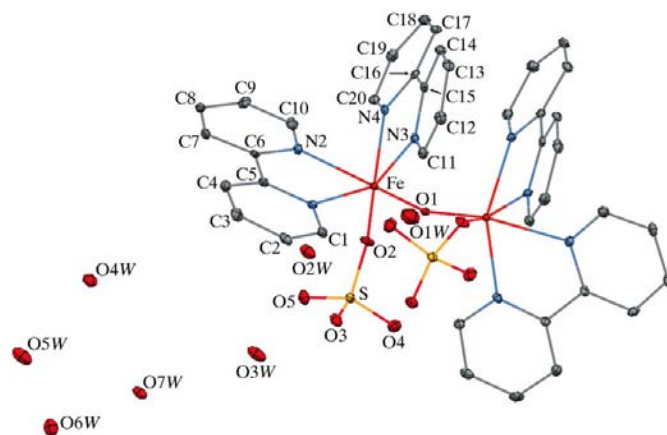
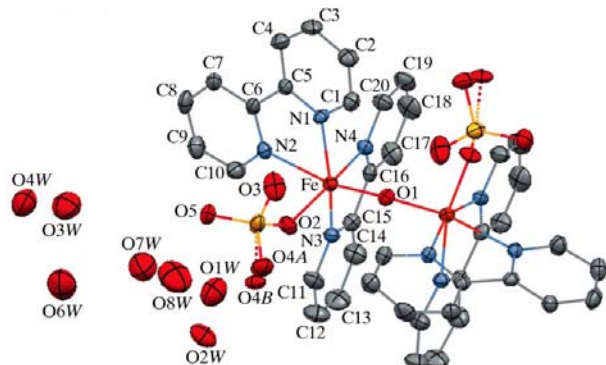


Figure 1
A view of the complex in (I). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity. Unlabelled atoms are related to labelled atoms by the symmetry operator $(2-x, y, \frac{1}{2}-z)$. Symmetry-generated solvent water molecules are not shown.

atoms (Fe, O1, O2, N2 and N4) are only approximately coplanar in both structures [r.m.s. deviation 0.2173 for (I) and 0.1890 Å for (II)]. The Fe–O–Feⁱ angle [symmetry code: (i) $-x + 2, y, -z + \frac{1}{2}$] deviates appreciably from linearity, with a value of 161.7 (2)° in (I) and 165.8 (2)° in (II). The Feⁱ··Feⁱ distance is 3.556 (4) Å in (I) and 3.544 (1) Å in (II). The corresponding values in the analogous phenanthroline complex (Odoko & Okabe, 2005) are 172.8 (1)° and 3.555 (2) Å.

A comparison between the structures of the dinuclear complex molecules in the two hydrates is in order. The two pyridyl rings of bpy are appreciably twisted with respect to each other in (I), while they are nearly coplanar in (II). The C4–C5–C6–C7 and C14–C15–C16–C17 torsion angles are, respectively, 7.5 (4) and 19.3 (4)° in (I), and –2.7 (6) and 1.3 (6)° in (II). These distortions are within the normal range of 0–26° seen in coordinated bpy ligands (Xiang *et al.*, 1998). The ligands in the two halves are disposed in such a manner as



● O5W

Figure 2

A view of the complex in (II). Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity. Disordered parts are indicated by broken bonds. Unlabelled atoms are related to labelled atoms by the symmetry operator $(2 - x, y, \frac{1}{2} - z)$. Symmetry-generated solvent water molecules are not shown.

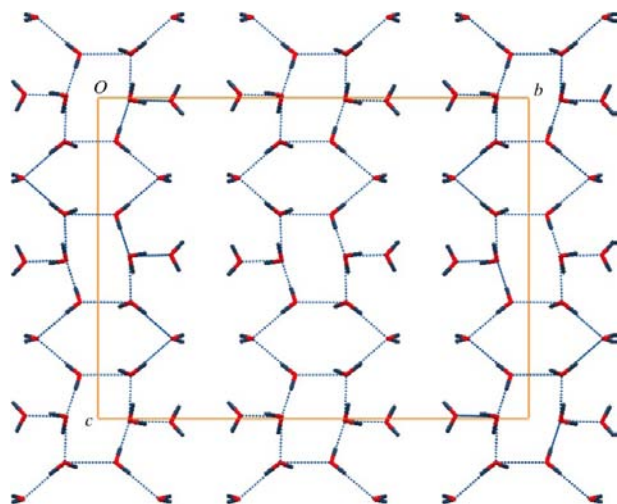


Figure 3

A view showing the hydrogen-bonded network of solvent water molecules in (I). Hydrogen-bond contacts are shown as dotted lines.

to reduce the repulsion between the sulfate ions without compromising the attractive π – π stacking interaction between the pyridyl rings. The O2–Fe–Feⁱ–O2ⁱ torsion angle is 123.4 (1)° in (I) and –116.7 (1)° in (II).

One pair of symmetry-related bpy ligands participates in intramolecular π – π stacking. This interaction is stronger in (I), with eight C··C contacts in the range 3.33–3.68 Å, while in (II) the contacts are all greater than 3.62 Å. The bpy molecules with the largest twist angle are involved in the intramolecular stacking of (I). Intermolecular stacking involving all the bpy ligands is observed in both structures, with several C··C contacts in the range 3.38–3.69 Å in (I) and 3.36–3.70 Å in (II). It is noteworthy that in (I), the bpy ligand having the largest twist angle is involved in intramolecular stacking as

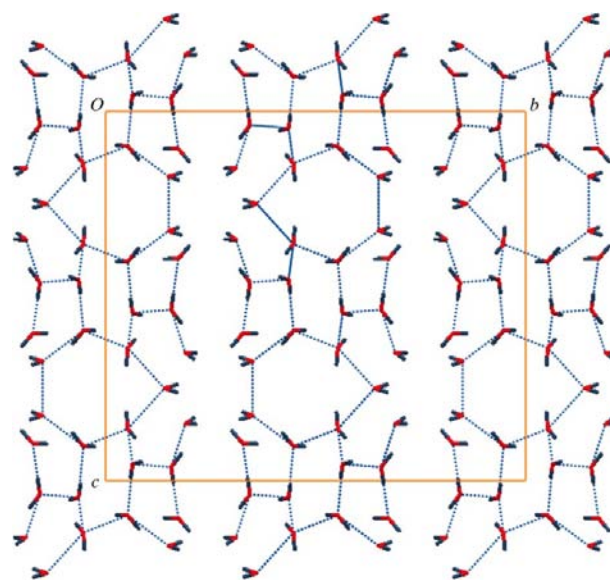


Figure 4

A view showing the hydrogen-bonded network of solvent water molecules in (II). Hydrogen-bond contacts are shown as dotted lines.

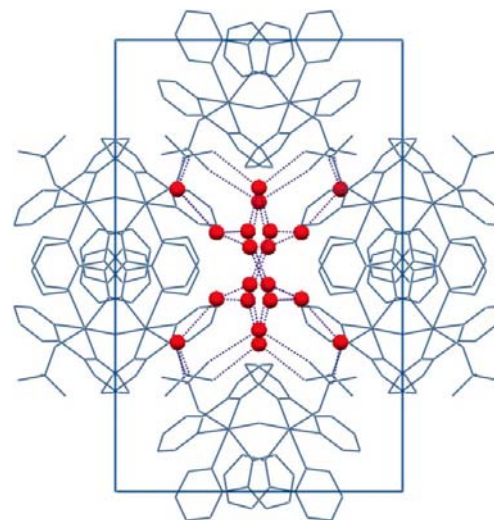


Figure 5

The unit-cell packing (*ab* plane) in compound (I). H atoms are not included. Hydrogen-bond contacts are shown as dotted lines and solvent water O atoms are shown as balls.

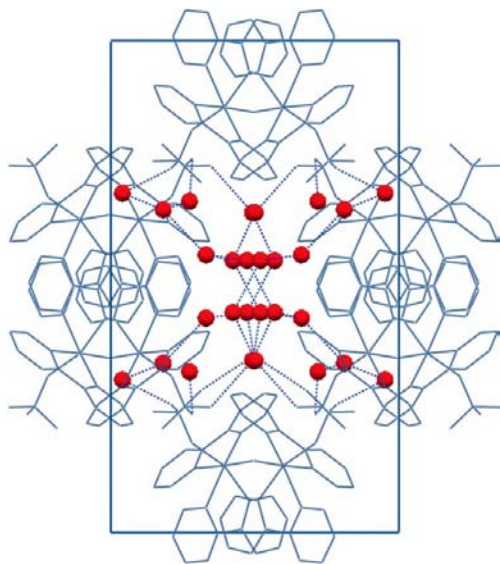


Figure 6
The unit-cell packing (*ab* plane) in compound (II). H atoms are not included. Hydrogen-bond contacts are shown as dotted lines and solvent water O atoms are shown as balls.

well as intermolecular stacking. It appears that the large twist facilitates this ‘conjugation’ of the two types of interactions.

Considering the crystal packing, in both compounds the complex molecules assemble together to produce oval-shaped channels, with an average diameter of about 6.5 Å along the *c* axis. The sulfate O atoms line the inside of these channels, while the hydrophobic parts of the bpy ligands are on the outside. The solvent water molecules forming hydrogen-bonded ribbons occupy these channels. The ribbons in (I) consists of two types of six-membered rings fused together, while in (II) there are alternate six- and seven-membered rings. In (I), there is an additional water molecule hydrogen-bonded to one six-membered ring (Fig. 3). In (II), there is a cluster of three water molecules interacting with each six-membered ring (Fig. 4). In both structures, the tapes are bonded to the channels through these extra water molecules *via* hydrogen-bonding interactions with sulfate O atoms (Figs. 5 and 6).

It is remarkable that the presence of sodium acetate or 1,2-diaminoethane in the reaction medium led to the formation of crystals of two different hydrates of a compound which has previously been obtained only as a precipitate. Other than adjusting the pH, the role of these substances, which are themselves coordinating ligands, in the crystallization process is not known.

Experimental

For the preparation of compound (I), ferric sulfate (0.800 g, 2.00 mmol) and sodium acetate (0.656 g, 8.00 mmol) were stirred in water (40 ml) and the mixture was heated on a water bath. 2,2'-Bipyridine (0.312 g, 2.00 mmol) was dissolved in ethanol (5 ml) and added to the hot solution. The mixture was stirred continuously and maintained at 353 K for 10 min. The small amount of light-brown precipitate that formed was filtered off and the brown-red solution

kept for crystallization. From this solution, shiny dark-red crystals of (I) formed after 10 d. CHN analysis calculated for C₄₀H₅₄Fe₂N₈O₂₀S₂: C 42.04, H 4.76, N 9.80, S 5.61; found C 42.03, H 4.58, N 9.81, S 5.54%. IR (KBr disk, cm⁻¹): 3400, 1645, 1599, 1495, 1474, 1440, 1317, 1109, 1022, 823, 767, 617.

Compound (II) was prepared by a similar method, but with 1,2-diaminoethane (0.165 ml, 2.36 mmol) used in place of sodium acetate. Wine-red crystals were formed after 10 d. CHN analysis calculated for C₄₀H₆₂Fe₂N₈O₂₄S₂: C 39.55, H 5.14, N 9.22, S 5.28; found C 39.61, H 5.11, N 9.24, S 5.18%. IR (KBr disk, cm⁻¹): 3400, 1645, 1599, 1495, 1475, 1441, 1317, 1149, 1022, 825, 769, 654.

Compound (I)

Crystal data

[Fe₂O(SO₄)₂(C₁₀H₈N₂)₄].11H₂O Z = 4
M_r = 1142.73 *D_x* = 1.585 Mg m⁻³
 Monoclinic, C2/c Mo Kα radiation
a = 13.7244 (8) Å *μ* = 0.78 mm⁻¹
b = 21.6461 (13) Å *T* = 100 (2) K
c = 16.1238 (9) Å Block, red
 β = 90.6800 (10)° 0.20 × 0.08 × 0.07 mm
V = 4789.7 (5) Å³

Data collection

Bruker SMART CCD area-detector 27533 measured reflections
 diffractometer 5757 independent reflections
 φ and ω scans 4601 reflections with *I* > 2σ(*I*)
 Absorption correction: multi-scan *R_{int}* = 0.069
 (SADABS; Sheldrick, 1996) *θ_{max}* = 28.3°
T_{min} = 0.783, *T_{max}* = 0.947

Refinement

Refinement on *F*² *w* = 1/[σ²(*F_o*²) + (0.0436*P*)²
R [*F*² > 2σ(*F*²)] = 0.060 + 10.7762*P*]
wR (*F*²) = 0.121 where *P* = (*F_o*² + 2*F_c*²)/3
S = 1.14 (Δ/σ)_{max} = 0.001
 5757 reflections Δρ_{max} = 0.70 e Å⁻³
 327 parameters Δρ_{min} = -0.42 e Å⁻³
 H-atom parameters constrained

Table 1

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

Fe—O1	1.8009 (6)	Fe—N3	2.160 (2)
Fe—O2	1.955 (2)	Fe—N4	2.186 (3)
Fe—N1	2.126 (2)	Fe—N2	2.296 (2)
Fe—O1—Fe ⁱ	161.67 (17)		

Symmetry code: (i) -*x* + 2, *y*, -*z* + ½.

Table 2

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

<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>
O1W—H1A...O2W	0.94	1.89	2.816 (4)	167
O1W—H1B...O6W ⁱⁱ	0.78	2.07	2.734 (4)	143
O2W—H2A...O5	0.92	1.91	2.824 (3)	170
O3W—H3A...O5	0.81	2.10	2.886 (3)	163
O4W—H4A...O4 ⁱⁱⁱ	0.87	1.98	2.849 (3)	172
O4W—H4B...O4 ^{iv}	0.85	2.00	2.838 (3)	168
O5W—H5A...O1W ⁱⁱⁱ	0.88	1.89	2.739 (4)	161
O5W—H5B...O4W	0.94	1.88	2.799 (3)	162
O6W—H6A...O5W	0.84	1.89	2.729 (4)	177
O6W—H6B...O7W	0.83	2.05	2.880 (3)	176
O7W—H7A...O3 ^{iv}	0.86	1.99	2.820 (3)	163

Symmetry codes: (ii) -*x* + ½, *y* + ½, -*z* + ½; (iii) *x* - ½, -*y* + ½, *z* - ½; (iv) -*x* + 1, *y*, -*z* + ½.

Compound (II)

Crystal data

[Fe ₂ O(SO ₄) ₂ (C ₁₀ H ₈ N ₂) ₄]·15H ₂ O	Z = 4
<i>M_r</i> = 1214.80	<i>D_x</i> = 1.502 Mg m ⁻³
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.8303 (18) Å	<i>μ</i> = 0.71 mm ⁻¹
<i>b</i> = 21.819 (3) Å	<i>T</i> = 298 (2) K
<i>c</i> = 19.312 (3) Å	Block, red
<i>β</i> = 96.288 (3)°	0.30 × 0.12 × 0.12 mm
<i>V</i> = 5373.6 (13) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	12439 measured reflections
<i>φ</i> and <i>ω</i> scans	5272 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	2798 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.738, <i>T_{max}</i> = 0.919	<i>R_{int}</i> = 0.094
	<i>θ_{max}</i> = 26.0°

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.057	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0091 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.107	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 0.84	(Δσ) _{max} < 0.001
5272 reflections	Δρ _{max} = 0.49 e Å ⁻³
353 parameters	Δρ _{min} = -0.31 e Å ⁻³

Table 3

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

Fe—O1	1.7860 (7)	Fe—N3	2.140 (3)
Fe—O2	1.965 (3)	Fe—N4	2.190 (3)
Fe—N1	2.132 (3)	Fe—N2	2.241 (3)
Fe—O1—Fe ⁱ	165.8 (2)		

Symmetry code: (i) -x + 2, y, -z + ½

Table 4

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

<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>
O1W—H1A...O3W ⁱⁱ	0.86	1.96	2.744 (5)	150
O1W—H1B...O5W ⁱⁱⁱ	0.87	2.42	2.887 (4)	115
O2W—H2A...O5 ^{iv}	0.83	2.04	2.843 (4)	163
O2W—H2B...O4A	0.73	2.10	2.797 (9)	160
O3W—H3A...O7W	0.72	2.10	2.825 (5)	177
O3W—H3B...O4W ^v	0.79	2.04	2.782 (5)	157
O4W—H4A...O6W ^v	0.85	1.97	2.816 (5)	179
O4W—H4B...O2W ^{iv}	0.88	2.05	2.825 (5)	146
O5W—H5A...O3 ^{iv}	0.86	2.22	2.864 (4)	132
O6W—H6A...O4A ^{iv}	0.85	2.04	2.884 (3)	176
O6W—H6B...O7W	0.83	2.45	3.277 (6)	173
O7W—H7A...O1W	0.90	2.01	2.717 (5)	134
O7W—H7B...O8W	0.94	1.88	2.774 (6)	159
O8W—H8A...O4B ^{iv}	0.89	2.24	3.131 (6)	179
O8W—H8B...O5	0.75	2.11	2.816 (5)	159

Symmetry codes: (ii) -x + 1, -y, -z; (iii) x + ½, y - ½, z; (iv) -x + 1, y, -z + ½; (v) -x + ½, -y + ½, -z.

In compound (II), one of the O atoms of the sulfate ion is disordered over two positions, denoted O4A and O4B, with occupancy factors of 0.73 and 0.27, respectively. H atoms were positioned geometrically and treated as riding, with C—H distances of 0.95 Å and O—H distances in the range 0.72–0.94 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,O).

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3017). Services for accessing these data are described at the back of the journal.

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