

Aquabis(tetrahydrofuran)hexakis(trifluoroacetato)(μ_3 -oxo)zinc(II)diiron(III)

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Key indicators

Single-crystal X-ray study

$T = 163\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

Disorder in main residue

R factor = 0.042

wR factor = 0.119

Data-to-parameter ratio = 12.5

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

In the oxo-centered compound, $[\text{ZnFe}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})]$, the central O atom is linked to three metal atoms, which are themselves each linked to four trifluoroacetate anions and are in a triangular configuration. Two of the metal atoms are each coordinated by a tetrahydrofuran molecule, whereas the third is coordinated by a water molecule. Two $[\text{ZnFe}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})]$ units are linked by a pair of hydrogen bonds across a center of inversion to afford a hydrogen-bonded dimer. The compound is isostructural with the $\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}_2$ analog.

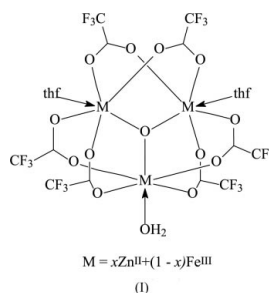
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Comment

The preceding report on the mixed-metal oxo-cluster carboxylate, $\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})$, described the intended purpose for a crystal structure study of the compound (Amini *et al.*, 2004). Replacing the Cu^{II} atom by another divalent atom, Zn^{II} , gave the isomorphous title compound, (I) (Fig. 1). Pairs of adjacent molecules are linked by hydrogen bonds into a centrosymmetric dimer (Fig. 2). The compound is isostructural with the Cu^{II} analog, and even the occupancies of the three metal atoms refined to Zn:Fe ratios [0.662 (2):0.338 (2), 0.191 (8):0.809 (8), and 0.146 (8):0.854 (8) for sites 1, 2 and 3, respectively] that are almost identical to those for the Cu^{II} compound, giving a preponderance of Zn on the site coordinated by water rather than tetrahydrofuran.



Experimental

The procedure for preparing the compound was adapted from that reported for the synthesis of $[\text{MFe}_2\text{O}(\text{O}_2\text{CCl}_3)(\text{THF})_3]$, where M is Mn, Co or Ni (Wang & Yu, 1990). Sodium bicarbonate (4.12 g, 49 mmol) was dissolved in water (45 ml) and this was mixed with trifluoroacetic acid (5.5 g, 48 mmol), ferric nitrate nonahydrate (6.46 g, 16 mmol) dissolved in water (15 ml) and zinc nitrate hexahydrate (2.37 g, 8 mmol) dissolved in water (5 ml). The mixture was stirred for 24 h and then at 333 K for a further 3 h. The water was removed under reduced pressure and the residue was dissolved in a mixture of tetrahydrofuran and hexane. The solution was filtered and the solvent removed to give an oily residue. This was treated with hexane to remove the oil; the pure compound was obtained by

recrystallization from hexane to which several drops of tetrahydrofuran were added. The red, almost brown, compound melts at 461–463 K.

Crystal data

[ZnFe₂O(C₂F₃O₂)₆(C₄H₈O)₂(H₂O)]
M_r = 1033.41
 Triclinic, *P* $\bar{1}$
a = 9.2200 (6) Å
b = 12.8671 (9) Å
c = 16.448 (1) Å
 α = 96.233 (1)°
 β = 105.756 (1)°
 γ = 99.401 (1)°
V = 1828.6 (2) Å³

Z = 2
D_x = 1.877 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6516 reflections
 θ = 2.5–26.4°
 μ = 1.59 mm⁻¹
T = 163 (2) K
 Plate, red
 0.40 × 0.40 × 0.08 mm

Data collection

Bruker *P4*/CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.519, *T_{max}* = 0.883
 21898 measured reflections

7257 independent reflections
 5760 reflections with *I* > 2σ(*I*)
R_{int} = 0.036
R_{max} = 26.5°
h = -11 → 11
k = -15 → 16
l = -20 → 19

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.119
S = 1.03
 7257 reflections
 581 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0593*P*)² + 2.3206*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.70 e Å⁻³
 Δρ_{min} = -0.67 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—O1	2.069 (3)	Fe2—O11	2.072 (3)
Zn1—O3	2.195 (3)	Fe2—O13	2.104 (3)
Zn1—O5	2.287 (3)	Fe2—O15	1.897 (2)
Zn1—O7	2.027 (3)	Fe3—O2	2.056 (3)
Zn1—O15	1.946 (2)	Fe3—O4	2.010 (3)
Zn1—O1w	2.003 (2)	Fe3—O10	2.052 (3)
Fe2—O6	2.041 (3)	Fe3—O12	2.054 (3)
Fe2—O8	2.021 (3)	Fe3—O14	2.105 (2)
Fe2—O9	2.044 (3)	Fe3—O15	1.893 (2)
O1—Zn1—O3	88.8 (1)	O8—Fe2—O15	96.3 (1)
O1—Zn1—O5	83.7 (1)	O9—Fe2—O11	90.3 (1)
O1—Zn1—O7	167.6 (1)	O9—Fe2—O13	84.1 (1)
O1—Zn1—O15	95.7 (1)	O9—Fe2—O15	95.5 (1)
O1—Zn1—O1w	84.9 (1)	O11—Fe2—O15	95.3 (1)
O3—Zn1—O5	168.4 (1)	O11—Fe2—O13	83.2 (1)
O3—Zn1—O7	94.0 (2)	O13—Fe2—O15	178.5 (1)
O3—Zn1—O15	95.5 (1)	O2—Fe3—O4	89.0 (1)
O3—Zn1—O1w	84.6 (1)	O2—Fe3—O10	90.5 (1)
O5—Zn1—O7	91.6 (1)	O2—Fe3—O12	166.9 (1)
O5—Zn1—O15	94.2 (1)	O2—Fe3—O14	83.3 (1)
O5—Zn1—O1w	85.9 (1)	O2—Fe3—O15	97.2 (1)
O7—Zn1—O15	96.1 (1)	O4—Fe3—O10	167.0 (1)
O7—Zn1—O1w	83.3 (1)	O4—Fe3—O12	86.5 (1)
O15—Zn1—O1w	179.4 (1)	O4—Fe3—O14	84.8 (1)
O6—Fe2—O8	90.9 (1)	O4—Fe3—O15	99.0 (1)
O6—Fe2—O9	88.8 (1)	O10—Fe3—O12	91.2 (1)
O6—Fe2—O11	166.4 (1)	O10—Fe3—O14	82.3 (1)
O6—Fe2—O13	83.2 (1)	O10—Fe3—O15	94.0 (1)
O6—Fe2—O15	98.3 (1)	O12—Fe3—O14	84.0 (1)
O8—Fe2—O9	168.1 (1)	O12—Fe3—O15	95.7 (1)
O8—Fe2—O11	87.2 (1)	O14—Fe3—O15	176.2 (1)
O8—Fe2—O13	84.1 (1)		

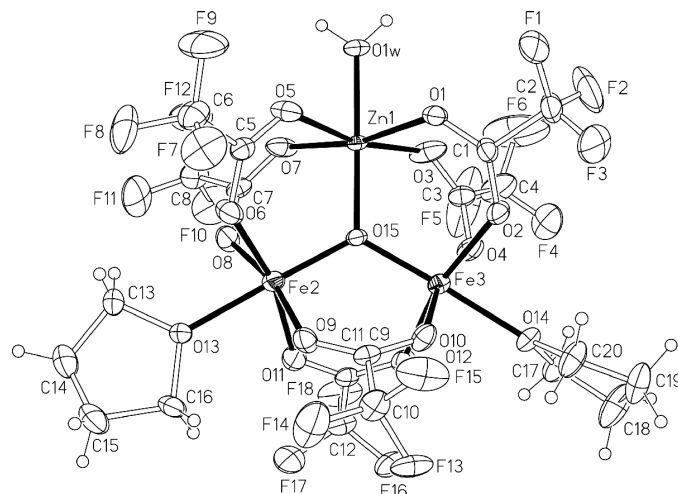


Figure 1 ORTEP (Johnson, 1976) plot of (I); displacement ellipsoids are drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii. Only one of the disordered components is shown for each CF₃ group. Zn1 shares the same site with Fe1 (not shown), Zn2 with Fe2 (not shown) and Zn3 with Cu3 (not shown); the labels here are in accordance with the predominant metal at each site.

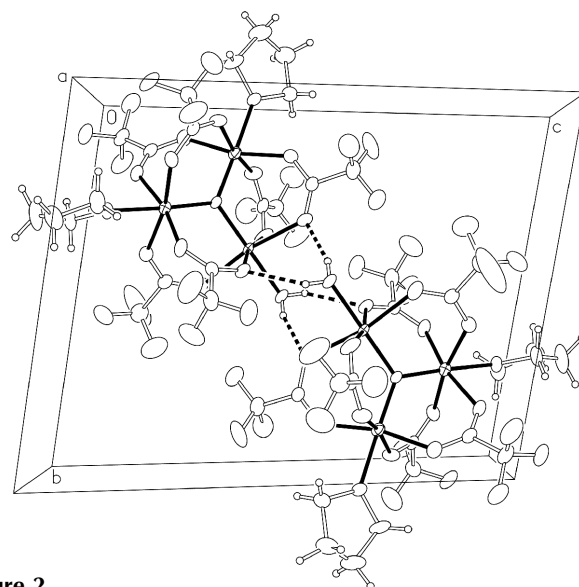


Figure 2 ORTEP (Johnson, 1976) plot of the hydrogen-bonded (I) dimer.

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

<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—H1w1...O1 ⁱ	0.85 (1)	2.34 (4)	2.961 (4)	131 (5)
O1w—H1w2...O5 ⁱ	0.84 (1)	2.04 (2)	2.843 (4)	159 (5)

Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.

Initial atomic coordinates were taken from those of the isomorphous Cu^{II}Fe^{III}₂ compound (Amini *et al.*, 2004). The water H atoms were located in a difference map and refined with an O—H restraint of 0.85 (1) Å. The other H atoms were placed in calculated positions (C—H = 0.99 Å), and they were included in the refinement in the riding model approximation; *U*_{iso}(H) = 1.2*U*_{eq}(C). Two of the six trifluoromethyl groups are disordered, and the occupancies of the F atoms were refined. For these groups, the C—F distances were

restrained to 1.32 (1) Å and the F··F distances to 2.16 (2) Å. The disordered atoms were restrained to be approximately isotropic. For each group, the six partial F atoms were restrained to be approximately coplanar. The disordered metal site occupancy factors were refined as for the Cu^{II}Fe^{III}₂ analog (Amini *et al.*, 2004).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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