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Key indicators

Single-crystal X-ray study
 $T = 163\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
Disorder in main residue
 R factor = 0.039
 wR factor = 0.109
Data-to-parameter ratio = 12.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Aquabis(tetrahydrofuran)hexakis(trifluoro-
acetato)(μ_3 -oxo)copper(II)diiron(III)

In the oxo-centered title compound, $[\text{CuFe}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})]$, 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 $[\text{CuFe}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})]$ units are linked by a pair of hydrogen bonds across a center of inversion to afford a hydrogen-bonded dimer.

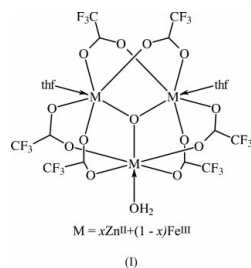
Comment

The mixed-metal and mixed-valence carboxylates represented by the formula $M^{\text{II}}M^{\text{III}}_2\text{O}(\text{O}_2\text{CR})_6L_3$, where L is a donor ligand, feature a central O atom that is covalently bonded to the three metal (M) atoms. The metal atoms themselves are each coordinated by four bridging carboxylate groups, and the octahedral geometry is completed by the donor ligand. The compound has no net charge if it has one M^{II} atom and two M^{III} atoms, but if the three M atoms are of the +3 type, the +1 charge is balanced by a counter-ion. The range of metal ions, carboxylate anions and donor ligands is enormous, and more than 250 such complexes have been crystallographically documented according to the November 2002 Version of the Cambridge Structural Database (Allen, 2002). Our interest in this class of triangular-shaped compounds arises from the report of the structure of the mixed-metal compound, $[\text{MnFe}_2\text{O}(\text{O}_2\text{CCl}_3)_6(\text{C}_4\text{H}_8\text{O})_3]$, which belongs to the trigonal space group $R\bar{3}m$ (Wang & Yu, 1990). The tetrahydrofuran-free compound separates from water when the Mn^{2+} , Fe^{3+} and $\text{Cl}_3\text{CCO}_2^-$ reagents are mixed and the tetrahydrofuran is incorporated when the compound is recrystallized from a pentane–tetrahydrofuran solvent system. In the compound, the central O atom occupies a special position of $3m$ site symmetry. However, the symmetry appears to be too high, because the three-coordinate O atom would have a perfectly planar environment, which in the absence of disorder is unlikely, as three-coordinate O is generally pyramidal. In another oxo-centered salt, $[\text{MnCr}_2\text{O}(\text{O}_2\text{CC}_6\text{H}_5)_6(\text{C}_5\text{H}_5\text{N})_3][\text{CrO}_3\text{Cl}]$ (both Mn and Cr in the +3 oxidation state in the oxocluster), the O atom has reported $\bar{6}$ site symmetry (Li *et al.*, 2002; Xu *et al.*, 1997), which again is too high. The correct space group of this compound is a lower one, $P6_3$ (Ng & Xie, 2003).

The title compound, (I), is the unexpected product that was obtained in the attempted synthesis of $[\text{CuFe}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_3]$, with trifluoroacetic acid as the carboxylic acid reagent in place of trichloroacetic acid. As noted in a large number of other trifluoroacetates (Gleghorn & Small, 1995), some of the trifluoromethyl groups in the present oxocluster compound are disordered. The structure

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represents another example of an oxocluster trifluoroacetate, for which only a few have been structurally characterized. These include $[\text{V}^{\text{II}}\text{V}^{\text{III}}\text{V}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_3]$ (Cotton *et al.*, 1982), $[\text{V}^{\text{II}}\text{V}^{\text{III}}\text{V}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_3] \cdot \frac{2}{3}\text{C}_4\text{H}_8\text{O} \cdot \frac{1}{3}\text{CH}_2\text{Cl}_2$ (Cotton *et al.*, 1986), $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{V}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (Ponomarev *et al.*, 1982) and $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{V}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_{18}\text{H}_{15}\text{-PO})_3]$ (Ponomarev *et al.*, 1986). The compound is also the first example of a mixed Cu/Fe triangular system.



The title compound contains a central O atom that is linked to three metal atoms arranged in a triangular configuration; each of the six carboxylate groups bridges two metal atoms. Two of the metal atoms are each coordinated by a tetrahydrofuran molecule whereas the third is coordinated by a water molecule (Fig. 1). Two $[\text{CuFe}_2\text{O}(\text{O}_2\text{CCF}_3)_6(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})]$ molecules are linked by a pair of hydrogen bonds across a center of inversion to afford a hydrogen-bonded dimer (Fig. 2). The crystalline compound turns opaque when left in the open, probably owing to the loss of either tetrahydrofuran or water, or both. It is not evident why the compound would include water in its coordination rather than a third tetrahydrofuran molecule; the incorporation of the tetrahydrofuran donor would probably lead to more efficient

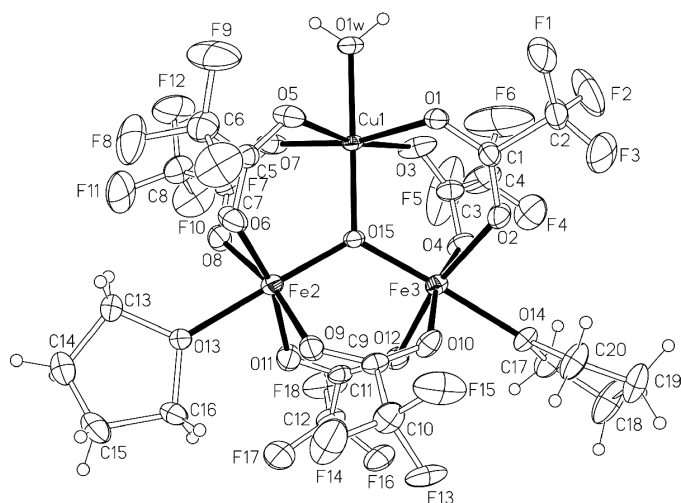


Figure 1
ORTEPII (Johnson, 1976) plot of (I); displacement ellipsoids are drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii. Only one of the disordered components is shown for each CF_3 group. The metal sites are labeled according to their preponderant occupancy. Cu1 shares the same site with Fe1 (not shown), Fe2 with Cu2 (not shown) and Fe3 with Cu3 (not shown).

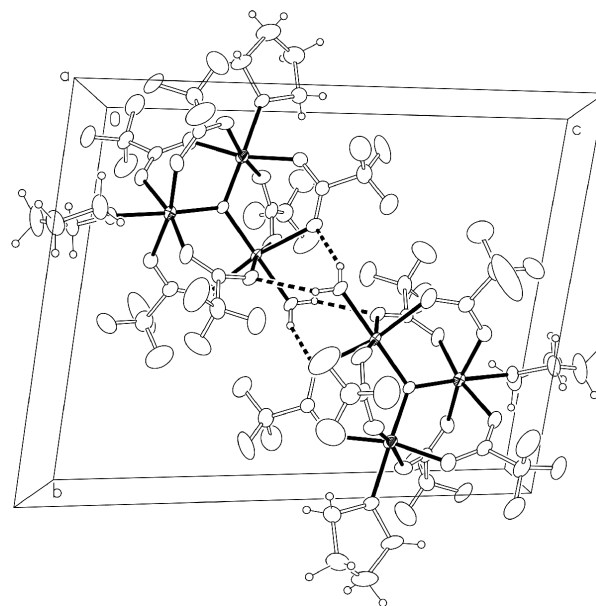


Figure 2
ORTEPII (Johnson, 1976) plot of the hydrogen-bonded (I) dimer.

packing, as the hypothetical compound could possibly crystallize in a much higher-symmetry space group.

Experimental

The procedure for preparing the compound was adapted from that reported for the synthesis of $M\text{Fe}_2\text{O}(\text{O}_2\text{CCl}_3)(\text{THF})_3$, where M is Mn, Co or Ni (Wang & Yu, 1990). To a solution (45 ml) of sodium bicarbonate (4.12 g, 49 mmol) was added trifluoroacetic acid (5.5 g, 48 mmol) followed by an aqueous (15 ml) solution of ferric nitrate nonahydrate (6.46 g, 16 mmol) and an aqueous (5 ml) solution of copper nitrate hexahydrate (2.36 g, 8 mmol). The mixture was stirred for 24 h and then warmed to 333 K for 3 h. The water was removed under reduced pressure and the residue dissolved in a THF–hexane mixture. After the solvent was removed, the oily residue obtained was washed several times with hexane to remove the oil. The solid that remained was recrystallized from hexane (20 ml) to which a few drops of THF were added. The crystals were of a deep orange, almost red, color; m.p. 432–434 K.

Crystal data

$[\text{CuFe}_2\text{O}(\text{C}_2\text{F}_3\text{O}_2)_6(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})]$
 $M_r = 1031.58$
Triclinic, $P\bar{1}$
 $a = 9.1773$ (6) Å
 $b = 12.8141$ (8) Å
 $c = 16.377$ (1) Å
 $\alpha = 96.216$ (1)°
 $\beta = 105.780$ (1)°
 $\gamma = 99.425$ (1)°
 $V = 1804.5$ (2) Å³

$Z = 2$
 $D_x = 1.899$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 6402 reflections
 $\theta = 2.5\text{--}26.4^\circ$
 $\mu = 1.54$ mm⁻¹
 $T = 163$ (2) K
Prism, orange
 $0.40 \times 0.30 \times 0.10$ mm

Data collection

Bruker P4/CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.684$, $T_{\text{max}} = 0.862$
22 910 measured reflections

7279 independent reflections
5780 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 26.6^\circ$
 $h = -7 \rightarrow 11$
 $k = -16 \rightarrow 16$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.109$
 $S = 1.00$
 7279 reflections
 581 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 2.3114P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.66 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.71 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

| | | | |
|-------------|-----------|-------------|-----------|
| Cu1—O1 | 2.059 (2) | Fe2—O11 | 2.062 (3) |
| Cu1—O3 | 2.183 (3) | Fe2—O13 | 2.091 (2) |
| Cu1—O5 | 2.276 (3) | Fe2—O15 | 1.888 (2) |
| Cu1—O7 | 2.017 (3) | Fe3—O2 | 2.044 (3) |
| Cu1—O15 | 1.936 (2) | Fe3—O4 | 2.002 (3) |
| Cu1—O1w | 1.996 (2) | Fe3—O10 | 2.042 (2) |
| Fe2—O6 | 2.033 (3) | Fe3—O12 | 2.040 (2) |
| Fe2—O8 | 2.013 (3) | Fe3—O14 | 2.096 (2) |
| Fe2—O9 | 2.032 (2) | Fe3—O15 | 1.889 (2) |
| O1—Cu1—O3 | 88.9 (1) | O8—Fe2—O15 | 96.2 (1) |
| O1—Cu1—O5 | 83.6 (1) | O9—Fe2—O15 | 95.5 (1) |
| O1—Cu1—O7 | 167.6 (1) | O9—Fe2—O11 | 90.2 (1) |
| O1—Cu1—O15 | 95.8 (1) | O9—Fe2—O13 | 84.2 (1) |
| O1—Cu1—O1w | 84.8 (1) | O11—Fe2—O13 | 83.3 (1) |
| O3—Cu1—O5 | 168.5 (1) | O11—Fe2—O15 | 95.2 (1) |
| O3—Cu1—O7 | 93.8 (1) | O13—Fe2—O15 | 178.4 (1) |
| O3—Cu1—O15 | 95.4 (1) | O2—Fe3—O4 | 89.0 (1) |
| O3—Cu1—O1w | 84.7 (1) | O2—Fe3—O10 | 90.5 (1) |
| O5—Cu1—O15 | 94.1 (1) | O2—Fe3—O12 | 166.9 (1) |
| O5—Cu1—O7 | 91.7 (1) | O2—Fe3—O14 | 83.3 (1) |
| O5—Cu1—O1w | 85.9 (1) | O2—Fe3—O15 | 97.2 (1) |
| O7—Cu1—O15 | 96.0 (1) | O4—Fe3—O10 | 166.9 (1) |
| O7—Cu1—O1w | 83.4 (1) | O4—Fe3—O12 | 86.4 (1) |
| O15—Cu1—O1w | 179.4 (1) | O4—Fe3—O14 | 84.8 (1) |
| O6—Fe2—O8 | 91.0 (1) | O4—Fe3—O15 | 99.0 (1) |
| O6—Fe2—O9 | 88.9 (1) | O10—Fe3—O14 | 82.2 (1) |
| O6—Fe2—O11 | 166.5 (1) | O10—Fe3—O12 | 91.2 (1) |
| O6—Fe2—O13 | 83.3 (1) | O10—Fe3—O15 | 94.1 (1) |
| O6—Fe2—O15 | 98.3 (1) | O12—Fe3—O14 | 84.0 (1) |
| O8—Fe2—O9 | 168.2 (1) | O12—Fe3—O15 | 95.7 (1) |
| O8—Fe2—O11 | 87.1 (1) | O14—Fe3—O15 | 176.2 (1) |
| O8—Fe2—O13 | 84.1 (1) | | |

Table 2
 Hydrogen-bonding geometry (\AA , $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| O1w—H1w1 \cdots O1 ⁱ | 0.84 (1) | 2.32 (4) | 2.947 (3) | 132 (5) |
| O1w—H1w2 \cdots O5 ⁱ | 0.84 (1) | 2.05 (2) | 2.824 (4) | 153 (4) |

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

The water H atoms were located in a difference map and refined with an O—H restraint of 0.85 (1) \AA . The other H atoms were placed in calculated positions (C—H = 0.95 \AA), and they were included in the refinement in the riding-model approximation; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Two of the six trifluoromethyl groups are disordered; the occupancies of the F atoms were refined. For the disordered groups, the C—F bonds were restrained to 1.32 (1) \AA and the F \cdots F distances to 2.16 (2) \AA . For each group, the six partial F atoms were restrained to be approximately coplanar. All three metal atom sites were refined with a mixed occupancy by Cu and Fe, with a restraint to give a total of one Cu and two Fe atoms; on each site a single set of displacement parameters was used. The refined occupancy factors for Cu and Fe on sites 1, 2 and 3 were 0.730 (2):0.270 (2), 0.151 (9):0.849 (9), and 0.118 (9):0.882 (9), respectively, giving a majority occupancy of Cu on site 1, which is coordinated by water.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (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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References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Cotton, F. A., Extine, M. X., Falvello, L. R., Lewis, D. B., Lewis, G. E., Murilo, C. A., Schwotzer, W., Tomas, M. & Troup, J. M. (1986). *Inorg. Chem.* **25**, 3503–3512.
 Cotton, F. A., Lewis, G. E. & Mott, G. N. (1982). *Inorg. Chem.* **21**, 3316–3321.
 Gleghorn, J. T. & Small, R. W. H. (1995). *Acta Cryst.* **B51**, 346–353.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Li, J. Y., Liu, P. & Qi, D. M. (2002). *Chem. Res.* **13**, 18–22.
 Ng, S. W. & Xie, Z. X. (2003). *Chin. J. Struct. Chem.* **22**, 691–699.
 Ponomarev, V. I., Filipenko, O. S., Atoyman, L. O., Bobkova, S. A. & Turte, K. I. (1982). *Dokl. Akad. Nauk SSSR*, **262**, 346–350; *Chem. Abstr.* **97**, 154244x.
 Ponomarev, V. I., Turte, K. I., Shilov, G. V., Bobkova, S. A., Atovmyan, L. O. & Stukan, R. A. (1986). *Koord. Khim.* **12**, 398–403; *Chem. Abstr.* **104**, 236114g.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Wang, Z.-M. & Yu, X.-F. (1990). *Chin. J. Struct. Chem.* **9**, 14–17.
 Xu, H., Li, J., Zou, J., Xu, Z., You, X., Guo, G., Huang, J. & Zhuang, H. (1997). *Polyhedron*, **16**, 1371–1375.