

## Two new soluble iron–oxo complexes: [Fe<sub>2</sub>(μ-O)(μ-O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>- (C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>] and [Fe<sub>4</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ- O<sub>2</sub>CCF<sub>3</sub>)<sub>6</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]- CF<sub>3</sub>CO<sub>2</sub>H

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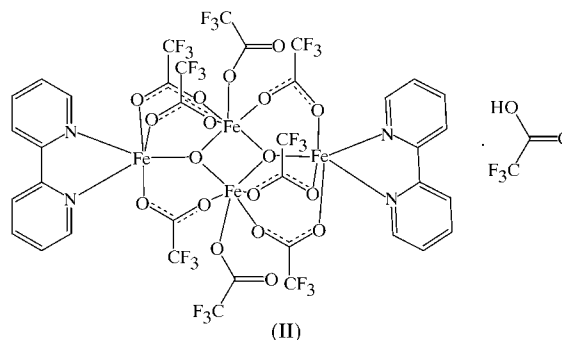
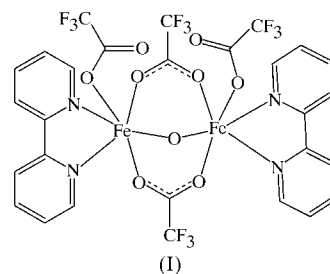
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Two new iron–oxo clusters, *viz.* di-μ-trifluoroacetato-μ-oxo-bis[(2,2'-bipyridine-κ<sup>2</sup>N,N')](trifluoroacetato-κO)iron(III), [Fe<sub>2</sub>O(CF<sub>3</sub>CO<sub>2</sub>)<sub>4</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>], and bis(2,2'-bipyridine)di-μ<sub>3</sub>-oxo-hexa-μ-trifluoroacetato-bis(trifluoroacetato)tetrairon(III) trifluoroacetic acid solvate, [Fe<sub>4</sub>O<sub>2</sub>(CF<sub>3</sub>CO<sub>2</sub>)<sub>8</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]-CF<sub>3</sub>CO<sub>2</sub>H, contain dinuclear and tetranuclear Fe<sup>III</sup> cores, respectively. The Fe<sup>III</sup> atoms are in distorted octahedral environments in both compounds and are linked by oxide and trifluoroacetate ions. The trifluoroacetate ions are either bridging (bidentate) or coordinated to the Fe<sup>III</sup> atoms *via* one O atom only. The fluorinated peripheries enhance the solubility of these compounds. Formal charges for all the Fe centers were assigned by summing valences of the chemical bonds to the Fe<sup>III</sup> atom.

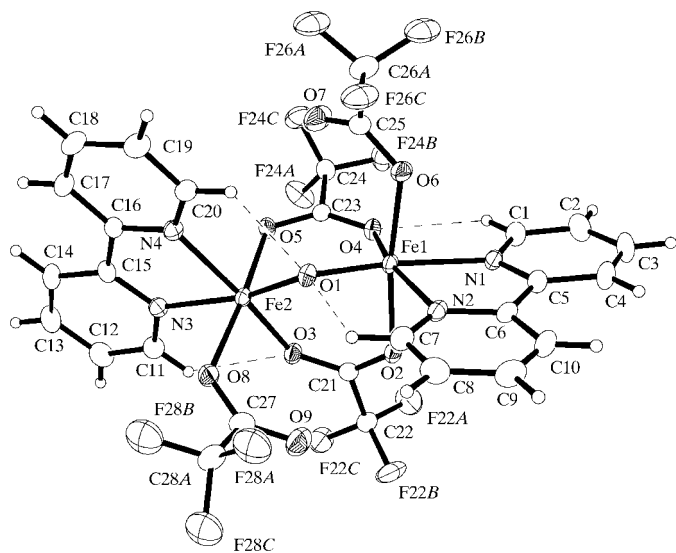
### Comment

Molecules containing two or more oxo-bridged Fe atoms have generated substantial interest and have been the subject of extensive investigation in a variety of contexts. These clusters exhibit interesting magnetic properties and have been found to behave as single-molecule magnets (Wernsdorfer & Sessoli, 1999). Moreover, polynuclear oxo-bridged iron units are located on the active sites of different proteins, and ferritin, the iron-storage protein found in most living organisms, contains a polynuclear oxo-iron(III) core (Gilles *et al.*, 2002). The active sites in hemerythrin and myohemerythrin, the oxygen transport proteins, have been shown to contain dinuclear Fe<sup>III</sup> cores bridged by oxide and carboxylate ions (Stenkamp *et al.*, 1984). An iron-based model compound for hemerythrin contains two Fe<sup>III</sup> atoms bridged by oxide and carboxylate ions (Lippard *et al.*, 1984). The typical hexacoordination of the iron centers in this cluster is completed by N atoms from imidazole groups. In Fe clusters, oxo, hydroxo and alkoxo bridges are prominent features because of the high

affinity of Fe atoms for oxygen-based ligands (Wilkinson *et al.*, 1988). We report here the structures of a new dinuclear iron–oxo complex, [Fe<sub>2</sub>(μ-O)(μ-O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>], (I), and a tetranuclear complex, [Fe<sub>4</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ-O<sub>2</sub>CCF<sub>3</sub>)<sub>6</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]-CF<sub>3</sub>CO<sub>2</sub>H, (II). The synthesis of (II) is unusual in that it was obtained using (I) as a building block. The fluorinated peripheries of (I) and (II) enhance the solubility of the compounds, as evidenced by the fact that both are soluble in acetone, tetrahydrofuran, acetonitrile, methanol, ethanol, nitromethane, dimethylformaldehyde and dimethyl sulfoxide. It is of interest to note that the trifluoroacetate ions are easily replaced by other ligands. Therefore, these compounds, together with suitable bridging ligands, can be used as precursors for new high-nuclearity clusters under mild reaction conditions. The iron centers are assigned a formal charge of +3 by summing the Fe–O bond valences (which are typical of Fe<sup>III</sup> atoms; Brown & Altermatt, 1985).



The molecular structure of (I) contains an [Fe<sub>2</sub>O]<sup>4+</sup> core bridged by an oxide ion and two trifluoroacetate groups (Fig. 1). Each Fe<sup>III</sup> atom is in a distorted octahedral environment and is coordinated to a μ-oxide ion, a 2,2'-bipyridine group and three trifluoroacetate ions. The *ortho* H atoms of the bipyridine unit donate hydrogen bonds to the bridging oxide ion and to the O atoms of the coordinated trifluoroacetate ions (C1–H1···O4, C7–H7···O1, C11–H11···O3 and C20–H20···O1; Table 2). These H atoms enhance the chelating nature of bipyridine and may even facilitate monodentate coordination of some of the trifluoroacetate ions. The 2,2'-bipyridine group is a capping ligand and is less labile than the trifluoroacetate ligands. Two of the four trifluoroacetate ions are bridging (and bidentate), while the other ions coordinate to the Fe<sup>III</sup> atom through one O atom. The trifluoro groups of the non-bridging trifluoroacetate ions are considerably disordered. The ordered trifluoroacetate groups accept weak (but important) hydrogen bonds from the bipyridyl units

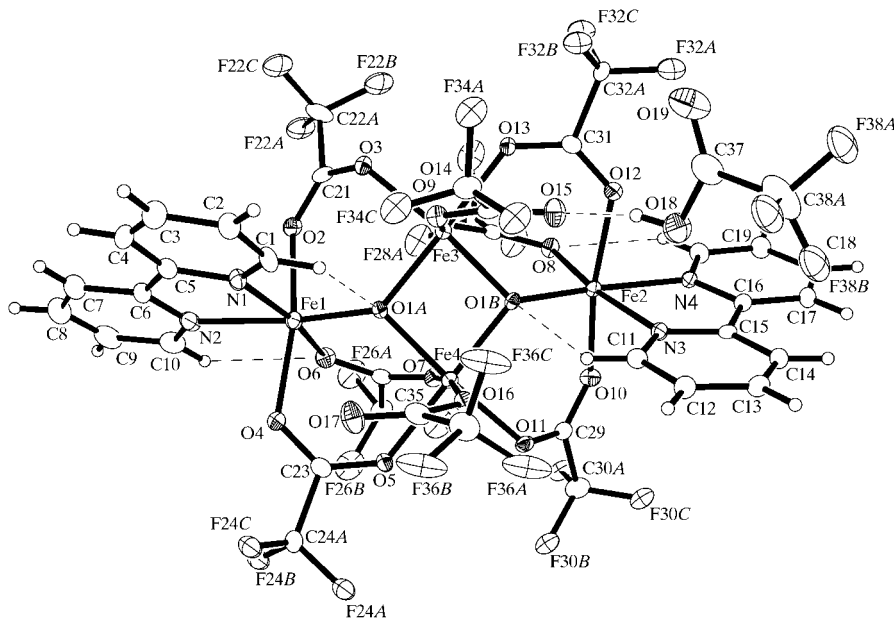

**Figure 1**

A displacement ellipsoid plot of (I). The bridging trifluoroacetate ions are disordered, but only one component of each disordered group is shown. Non-H atoms are represented by ellipsoids at the 50% probability level and H atoms are shown as circles with arbitrary radii.

(C20—H20···F22A<sup>i</sup>, C2—H2···F22C<sup>iii</sup>, C12—H12···F24A<sup>iv</sup>, C12—H12···F24B<sup>v</sup> and C10—H10···F24C<sup>vi</sup>; symmetry codes are given in Table 2). This behavior contrasts with that of the methyl groups of acetate ions, which normally donate hydrogen bonds. Thus the trifluoroacetate groups in (I) are anionic rather than cationic. The bridging trifluoroacetate groups are disordered in a complicated manner; there is rotational disorder as well as displacement of the C—C axes. This disorder was modeled using three separate  $-CF_3$  components for each disordered  $-CF_3$  group (including C

atoms), with C—F and F···F distances restrained to be equal in order to maintain tetrahedral geometry, and refined. Only one component of the disorder is shown in Fig. 1. The C—O bond distances [1.246 (3)–1.252 (3) Å; Table 1] of the bridging trifluoroacetate ions correspond to intermediate single and double bonds, while the C—O bond distances [1.213 (3) and 1.272 (3) Å] belonging to monodentate trifluoroacetate ions correspond to C—O single and double bonds. The complex is neutral and contains two Fe<sup>III</sup> centers and an oxide ion. All four trifluoroacetate groups are deprotonated. The Fe···Fe separation is 3.1492 (6) Å, which is typical for dinuclear Fe<sup>III</sup> complexes with bridging oxo and carboxylate groups (Christou *et al.*, 2000). The bridging groups across the Fe···Fe internuclear axis are nearly eclipsing, with O—Fe—Fe—O torsion angles of 17.45 (8) and 16.31 (8)°. This conformation is, in part, a consequence of the rigidity of the O—C—O bond angles, which cannot accommodate a staggered arrangement across these two Fe<sup>III</sup> atoms. The bridging carboxylate ligands also have an effect on the orientation of the two FeO<sub>4</sub>N<sub>2</sub> coordination polyhedra. These two corner-sharing octahedra are tilted towards one another, with a dihedral angle between the N1/N2/Fe1/O1/O4 and N3/O8/Fe2/O1/O5 square planes of 35.73 (7)°.

The molecular structure of (II) contains an [Fe<sub>4</sub>O<sub>2</sub>]<sup>4+</sup> core bridged by two  $\mu_3$ -oxide and six trifluoroacetate ions (Fig. 2 and Table 3). All Fe<sup>III</sup> atoms are in distorted octahedral environments. The two outer Fe<sup>III</sup> atoms, Fe1 and Fe2, are coordinated to the 2,2'-bipyridine group, a  $\mu_3$ -oxide and three bridging trifluoroacetate ions. As in (I), the H atoms *ortho* to the N atoms of the bipyridine group form hydrogen bonds with the bridging oxide ions and the O atoms of the coordinated trifluoroacetate ions (C1—H1···O1A, C10—H10···O6, C11—H11···O1B and C20—H20···O8; Table 4). The trifluoroacetic acid solvent molecule of crystallization acts as a hydrogen-bond donor to an O atom of a coordinated trifluoroacetate ion (O18—H18A···O15). All the trifluoroacetate groups are disordered and only one component of this disorder is shown in Fig. 2. Each of the two inner Fe<sup>III</sup> atoms, *viz.* Fe3 and Fe4, is coordinated to two  $\mu_3$ -oxide ions, three bridging trifluoroacetate ions and one monodentate trifluoroacetate ion. Several clusters containing [Fe<sub>4</sub>O<sub>2</sub>]<sup>4+</sup> cores have been reported in the literature, but the two inner Fe<sup>III</sup> atoms are usually bridged by carboxylate groups. In this new compound, the two Fe<sup>III</sup> atoms are bridged by two oxide ions. The core is non-planar, with the Fe1/Fe3/Fe4 and Fe2/Fe3/Fe4 planes forming a dihedral angle of 28.76 (3)°. The two inner Fe<sup>III</sup> atoms and two  $\mu_3$ -oxide ions, however, are nearly coplanar.


**Figure 2**

A displacement ellipsoid plot of (II). The trifluoroacetate groups are disordered, but only one component of each disordered group is shown. Non-H atoms are represented by ellipsoids at the 30% probability level and H atoms are shown as circles with arbitrary radii.

Atoms O1A and O1B are displaced 0.053 (11) Å from the Fe3/Fe4/O1A/O1B plane. The [Fe<sub>4</sub>O<sub>2</sub>]<sup>4+</sup> core has no imposed crystallographic symmetry, even though a core of this type might be expected to have *D*<sub>2h</sub> or *C*<sub>2</sub> symmetry. This absence of symmetry is a consequence of the two pairs of Fe<sup>III</sup> atoms Fe1 and Fe4, and Fe2 and Fe3, being bridged by two carboxylate groups each, while the two pairs Fe1 and Fe3, and Fe2 and Fe4, are bridged by a single carboxylate ligand each. The distances between atoms Fe1 and Fe4 [3.3063 (9) Å], and Fe2 and Fe3 [3.3131 (11) Å], are therefore shorter than the distances between atoms Fe1 and Fe3 [3.4735 (11) Å], and Fe2 and Fe4 [3.4505 (12) Å]. The shortest Fe···Fe separation [Fe3···Fe4 = 2.8934 (11) Å] occurs between the two inner Fe<sup>III</sup> atoms and is typical for [Fe<sub>4</sub>O<sub>2</sub>]<sup>4+</sup> clusters.

It is worth noting some of the differences between acetate and trifluoroacetate ions. Replacing electropositive H atoms with F atoms results in a reduction of the negative charge on the carboxylate O atoms, weaker coordination bonds to metal cations and slightly longer C—C bond distances. The carboxylate groups reduce the negative charge on the F atoms. These F atoms have slight anionic character and form weak intermolecular bonds, and therefore CF<sub>3</sub> groups are typically disordered.

Magnetic data clearly indicate that both complexes exhibit an *S* = 0 ground state, which arises from antiferromagnetic coupling of the Fe<sup>III</sup> atoms. As the temperature is increased, an increase in the effective moment of the complex is observed, which is due to thermal population of spin states with *S* greater than 0.

## Experimental

A suspension of FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (0.48 g, 1.0 mmol), 2,2'-bipyridine (0.16 g, 1.0 mmol), and NaO<sub>2</sub>CCF<sub>3</sub> (0.82 g, 6.0 mmol) in acetone (50 ml) was stirred for 24 h at room temperature under an atmosphere of dry air, resulting in an orange solution and a precipitate of NaCl. The precipitate was removed by filtration and the solvent was evaporated. The product was dissolved in acetone (20 ml), the solution filtered and excess diethyl ether added to the filtrate, giving a red-brown crystalline solid. The solid was extracted with tetrahydrofuran and layered with hexanes. Green crystals of (I) suitable for X-ray analysis were obtained after two or three days. A solution of (I) (0.10 g) dissolved in CF<sub>3</sub>COOH (5 ml) was stirred for 12 h, yielding a green-brown solution and an off-white precipitate. The precipitate was removed by filtration and the filtrate was evaporated slowly at room temperature. Red block-shaped crystals of (II) were collected by filtration, washed with hexanes and dried under vacuum.

## Compound (I)

### Crystal data

[Fe<sub>2</sub>O(C<sub>2</sub>F<sub>3</sub>O<sub>2</sub>)<sub>4</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 892.15  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*  
*a* = 10.3902 (16) Å  
*b* = 16.751 (3) Å  
*c* = 18.960 (3) Å  
 β = 98.046 (4)°  
*V* = 3267.4 (9) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.814 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1562 reflections  
 θ = 2.3–25.3°  
 μ = 1.02 mm<sup>-1</sup>  
*T* = 110 (2) K  
 Rectangular plate, pale green  
 0.40 × 0.28 × 0.06 mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 ω scans  
 Absorption correction: multi-scan (*SADABS*; Bruker, 2000)  
*T*<sub>min</sub> = 0.627, *T*<sub>max</sub> = 0.942  
 23 339 measured reflections  
 6984 independent reflections

5087 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.037  
 θ<sub>max</sub> = 27.5°  
*h* = -13 → 13  
*k* = -20 → 19  
*l* = -24 → 23

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.043  
*wR*(*F*<sup>2</sup>) = 0.118  
*S* = 1.04  
 6984 reflections  
 529 parameters  
 H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0535*P*)<sup>2</sup> + 2.838*P*]  
 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.65 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.58 e Å<sup>-3</sup>

**Table 1**

Selected interatomic distances (Å) for (I).

|         |             |        |             |
|---------|-------------|--------|-------------|
| Fe1—O1  | 1.7793 (17) | Fe2—O5 | 2.1440 (18) |
| Fe1—O6  | 1.9987 (18) | Fe2—N3 | 2.177 (2)   |
| Fe1—O4  | 2.0403 (19) | O3—C21 | 1.252 (3)   |
| Fe1—N2  | 2.122 (2)   | O2—C21 | 1.246 (3)   |
| Fe1—O2  | 2.1384 (19) | O5—C23 | 1.249 (3)   |
| Fe1—N1  | 2.177 (2)   | O4—C23 | 1.250 (3)   |
| Fe1—Fe2 | 3.1492 (6)  | O6—C25 | 1.270 (3)   |
| O1—Fe2  | 1.7780 (17) | O7—C25 | 1.213 (3)   |
| Fe2—O8  | 1.9894 (19) | O8—C27 | 1.272 (3)   |
| Fe2—O3  | 2.0664 (19) | O9—C27 | 1.215 (4)   |
| Fe2—N4  | 2.134 (2)   |        |             |

**Table 2**

Hydrogen-bonding 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> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C1—H1···O4                   | 0.95        | 2.49          | 3.059 (3)             | 119                     |
| C7—H7···O1                   | 0.95        | 2.54          | 3.062 (3)             | 115                     |
| C20—H20···O1                 | 0.95        | 2.50          | 3.028 (3)             | 115                     |
| C11—H11···O3                 | 0.95        | 2.57          | 3.145 (3)             | 119                     |
| C20—H20···F22A <sup>i</sup>  | 0.95        | 2.79          | 3.251 (3)             | 111                     |
| C17—H17···F22B <sup>ii</sup> | 0.95        | 2.64          | 3.428 (3)             | 141                     |
| C2—H2···F22C <sup>iii</sup>  | 0.95        | 2.58          | 3.257 (3)             | 128                     |
| C12—H12···F24A <sup>iv</sup> | 0.95        | 2.61          | 3.095 (3)             | 112                     |
| C12—H12···F24B <sup>v</sup>  | 0.95        | 2.45          | 3.284 (3)             | 146                     |
| C10—H10···F24C <sup>vi</sup> | 0.95        | 2.45          | 3.271 (3)             | 144                     |

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

## Compound (II)

### Crystal data

[Fe<sub>4</sub>O<sub>2</sub>(C<sub>2</sub>F<sub>3</sub>O<sub>2</sub>)<sub>8</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·  
 C<sub>2</sub>HF<sub>3</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 1585.96  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*  
*a* = 12.733 (3) Å  
*b* = 19.015 (4) Å  
*c* = 22.222 (4) Å  
 β = 91.63 (3)°  
*V* = 5378 (2) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.959 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 2413 reflections  
 θ = 2.3–26.6°  
 μ = 1.23 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Block, red-brown  
 0.35 × 0.27 × 0.19 mm

## Data collection

|  |  |
|--|--|
| Bruker SMART 1000 CCD area-detector diffractometer       | 10 470 independent reflections         |
| $\omega$ scans   | 7787 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $R_{\text{int}} = 0.040$               |
| $T_{\text{min}} = 0.670$ , $T_{\text{max}} = 0.803$      | $\theta_{\text{max}} = 26.9^\circ$     |
| 24 224 measured reflections                              | $h = -14 \rightarrow 16$               |
|  | $k = -24 \rightarrow 21$               |
|  | $l = -25 \rightarrow 28$               |

## Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 19.8269P]$           |
| $R[F^2 > 2\sigma(F^2)] = 0.060$ | where $P = (F_o^2 + 2F_c^2)/3$                               |
| $wR(F^2) = 0.136$               | $(\Delta/\sigma)_{\text{max}} = 0.001$                       |
| $S = 1.07$                      | $\Delta\rho_{\text{max}} = 0.85 \text{ e } \text{\AA}^{-3}$  |
| 10 470 reflections              | $\Delta\rho_{\text{min}} = -0.60 \text{ e } \text{\AA}^{-3}$ |
| 972 parameters                  |  |
| H-atom parameters constrained   |  |

**Table 3**

Selected interatomic distances ( $\text{\AA}$ ) for (II).

|         |             |         |             |
|---------|-------------|---------|-------------|
| Fe1—O1A | 1.837 (3)   | Fe2—Fe4 | 3.4502 (11) |
| Fe1—O6  | 2.031 (3)   | Fe3—O1B | 1.916 (3)   |
| Fe1—O4  | 2.062 (3)   | Fe3—O1A | 1.960 (3)   |
| Fe1—O2  | 2.068 (3)   | Fe3—O14 | 2.002 (3)   |
| Fe1—N1  | 2.107 (4)   | Fe3—O3  | 2.029 (3)   |
| Fe1—N2  | 2.148 (4)   | Fe3—O13 | 2.049 (3)   |
| Fe1—Fe4 | 3.3059 (11) | Fe3—O9  | 2.102 (3)   |
| Fe1—Fe3 | 3.4738 (11) | Fe3—Fe4 | 2.8934 (11) |
| Fe2—O1B | 1.840 (3)   | Fe4—O1A | 1.922 (3)   |
| Fe2—O8  | 2.030 (3)   | Fe4—O1B | 1.953 (3)   |
| Fe2—O10 | 2.042 (3)   | Fe4—O16 | 1.974 (3)   |
| Fe2—O12 | 2.052 (3)   | Fe4—O11 | 2.032 (3)   |
| Fe2—N3  | 2.097 (4)   | Fe4—O5  | 2.046 (3)   |
| Fe2—N4  | 2.117 (4)   | Fe4—O7  | 2.121 (3)   |
| Fe2—Fe3 | 3.3128 (11) |         |             |

**Table 4**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

| $D-H\cdots A$         | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------|-------|-------------|-------------|---------------|
| O18—H18A $\cdots$ O15 | 0.84  | 1.82        | 2.637 (5)   | 164           |
| C1—H1 $\cdots$ O1A    | 0.95  | 2.58        | 3.094 (6)   | 114           |
| C1—H1 $\cdots$ O14    | 0.95  | 2.38        | 3.217 (6)   | 146           |
| C10—H10 $\cdots$ O6   | 0.95  | 2.56        | 3.118 (7)   | 118           |
| C20—H20 $\cdots$ O8   | 0.95  | 2.52        | 3.083 (6)   | 118           |
| C11—H11 $\cdots$ O1B  | 0.95  | 2.59        | 3.109 (6)   | 115           |

Difference electron-density syntheses revealed disorder for the  $\text{CF}_3$  groups belonging to non-bridging trifluoroacetate ions in (I) and for all trifluoroacetate ions in (II). This disorder was modeled with the following approach: initially, the C—F and F $\cdots$ F distances were restrained to typical values [1.33 (1) and 2.14 (1)  $\text{\AA}$ ] for  $\text{CF}_3$  groups, obtained from a limited search of the Cambridge Structural Database (Allen, 2002). These values were refined once the disorder model was complete. Refinement of the model with these restraints and with site occupancies of 0.5 gave  $\text{CF}_3$  groups with sensible geometries. However, large peaks (1.55–4.53  $\text{e } \text{\AA}^{-3}$ ) in the difference syntheses indicated that each disordered  $\text{CF}_3$  group occupies two or more positions. Initially, these peaks were used to add F atoms belonging to a second component to each disordered  $\text{CF}_3$  group. The C atom of the ideal  $\text{CF}_3$  group was duplicated and the displacement parameters of both components were constrained to be equal. After refinement, there were two separate  $\text{CF}_3$  groups, rotated (and displaced slightly) about the first, with refined site occupancies of 0.5 (1). Large peaks (the highest being 2.48  $\text{e } \text{\AA}^{-3}$ ), seemingly belonging to third components,

were present. Three components were added to all bridging  $\text{CF}_3$  groups in (I) and to seven of the nine  $\text{CF}_3$  groups in (II). The C—F and F $\cdots$ F distances were restrained to be equal to one another and these values were refined. The maximum residual electron density in the regions of the  $\text{CF}_3$  groups was approximately equal to the largest peaks found elsewhere in the structure after isotropic refinement with this model, but anisotropic refinement resulted in prolate ellipsoids for these F atoms. Therefore, this disorder may be better represented by a large number of components or a torus of electron density about the C—C bond axis, with total occupancy equal to three F atoms. Because of the large number of disordered groups, the high number of parameters and free variables, and the weak scattering by each component, the maximum number of components in the disorder model was limited to three (with site occupancies refined and prolate ellipsoids representing the diffuse electron density). It was necessary to restrain the C—C bond distances in each component to be equal. Introducing the disorder model reduced the values of  $R1$  appreciably [from above 0.10 to 0.0431 for (I) and from above 0.12 to 0.0603 for (II)]. Refinement with the disorder model accounted for most of the electron density, with the highest peaks being similar in magnitude to the deepest holes. In (I), the highest residual peak is located 0.58  $\text{\AA}$  from atom F28B, and in (II), the highest peak is 0.68  $\text{\AA}$  from atom F24B. The H atom belonging to the carboxy group in (II) was placed at a position where it could donate a hydrogen bond to atom O15, with the C—O—H angle restrained to be tetrahedral.

For both compounds, data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1034). Services for accessing these data are described at the back of the journal.

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