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A polymeric form of basic iron(III) acetate with an acetic acid ligand

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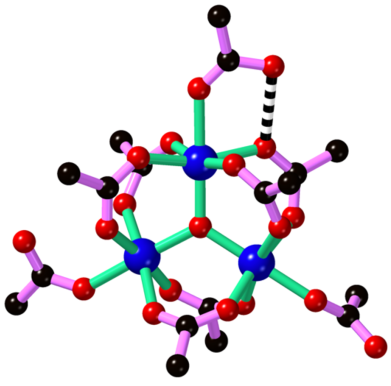
A new crystalline compound, *catena*-poly[hexa-μ-acetato-(acetic acid)-μ_3-oxido-*triangulo*-triiron(III)]-μ-acetato], $[Fe_3(C_2H_3O_2)_7O(C_2H_4O_2)]_n$, incorporating the basic ferric acetate unit, has been obtained from an acetic anhydride solution of hydrated iron(III) nitrate. The crystals have the composition $Fe_3O(OAc)_7$-(HOAc) (HOAc is acetic acid) and include the well-known $[Fe_3O(OAc)_6]^+$ unit, in which the Fe^{III} centres are linked to a central coplanar μ_3-oxido ligand. Acetate ions provide bridges between pairs of Fe^{III} centres. These individual $[Fe_3O(OAc)_6]^+$ units are linked by additional bridging acetate anions to form zigzag chains. The bridging acetate ions coordinate to a position *trans* to the oxido group on two of the Fe^{III} centres. Remarkably, the *trans* site on the third Fe^{III} centre is occupied by the carbonyl group of an acetic acid molecule. This is the first reported case of an acetic acid molecule coordinating to an Fe^{III} centre. Not surprisingly, the acetic acid molecule is only weakly coordinating, resulting in a short Fe—O(oxido) bond *trans* to the carbonyl group. The *trans* influence apparent in this structure provides an interesting contrast with the structurally similar Mn^{III} analogue, in which the corresponding pair of *trans* bonds are both elongated because of the Jahn–Teller effect.

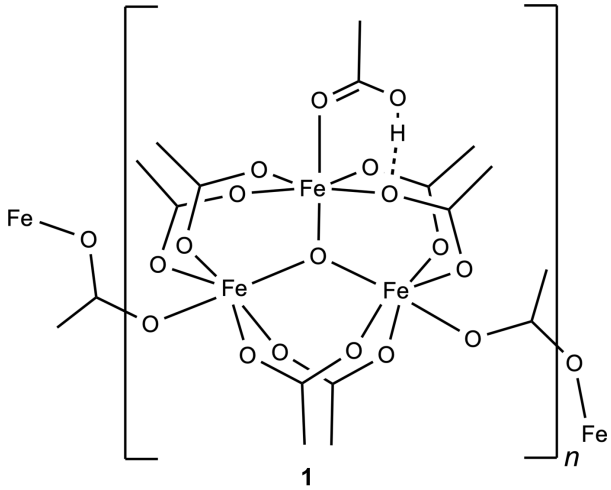
1. Introduction

In the field of coordination chemistry, carboxylate ions feature prominently in the formation of a wide variety of metal complexes. Although the carboxylate group is capable of chelation, it is not a strongly favoured coordination mode because of the strain associated with the four-membered ring. It is far more common for the carboxylate ion to span a pair of metal centres, as it does in complexes such as copper acetate, where four bridging acetate anions bridge a pair of Cu^{II} centres (van Niekerk & Schoening, 1953). A similar structure is adopted by molybdenum acetate, which features a remarkable quadruple bond between the Mo^{II} centres (Lawton & Mason, 1965; Cotton *et al.*, 2005). In the case of basic zinc acetate, four Zn^{II} centres, at the vertices of a tetrahedron, are bound to a central oxido anion (μ_4), while six acetate anions bridge pairs of Zn^{II} centres along the six edges of the tetrahedron (Wyart, 1926). The six methyl groups are oriented outwards towards the vertices of an octahedron. Basic beryllium acetate adopts a similar structure (Pauling & Sherman, 1934).

The basic ferric acetate cation contains the $[Fe_3O(OAc)_6]^+$ unit and consists of a planar μ_3-oxido group bound to a trio of Fe^{III} centres at the vertices of what is essentially an equilateral triangle (*e.g.* Anson *et al.*, 1987; Balić *et al.*, 2021; Abánades Lázaro *et al.*, 2023). Each pair of Fe^{III} centres is bridged by a pair of acetate anions, one above and one below the plane of the Fe_3O entity, to give a unit which has approximate D_{3h} symmetry. The site *trans* to the oxido group on each metal is



typically occupied by a monodentate ligand such as water. The methyl groups in this complex are directed towards the vertices of a trigonal prism. This type of unit may also be generated with trivalent Cr (Figgis & Robertson, 1965), Mn (Hessel & Romers, 1969) and Ru (Nikolaou *et al.*, 2023) centres, and can also exist for metals in mixed +2 and +3 oxidation states (Sato *et al.*, 1996; Wei *et al.*, 2020). Within the Cambridge Structural Database (CSD; Version 5.45, March 2024 release; Groom *et al.*, 2016), 83 structures have been reported which contain the $[Fe_3O(OAc)_6L_3]$ unit, where *L* may be a neutral or charged ligand. The net charge on the $[Fe_3O(OAc)_6L_3]$ complex is typically balanced by a non-coordinating ion, such as chloride or perchlorate.



1

Scheme 1

In the current work, we report the serendipitous isolation of basic ferric acetate crystals which display a significant distortion from the symmetric oxido bridge that is commonly observed with basic ferric carboxylate structures and rationalize this reduced symmetry in terms of a significant *trans* influence.

2. Experimental

2.1. Synthesis and crystallization

In an attempt to prepare Fe-based coordination polymers incorporating the dianion of hydroxybenzoic acid (H_2hba), three acetic anhydride (Ac_2O) solutions were prepared. Fe$(NO_3)_3\cdot 9H_2O$ (202 mg) was dissolved in Ac_2O (3 ml), H_2hba (110 mg) was dissolved in Ac_2O (2 ml) and LiOAc (255 mg) was dissolved in Ac_2O (3 ml). The solutions were mixed and heated to boiling on a hotplate. Small red–brown crystals were obtained from the cooled solution.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were placed in calculated positions and refined as riding atoms, with U_{iso}(H) = 1.5U_{eq}(C) and C—H = 0.99 Å for methyl groups, and U_{iso}(H) = 1.5U_{eq}(O) and O—H = 0.85 Å for the hydroxy H atom.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Fe_3(C_2H_3O_2)_7O(C_2H_4O_2)]$
M_r	656.91
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, *b*, *c* (Å)	15.8661 (3), 15.8640 (3), 19.5003 (5)
V (Å^3)	4908.22 (18)
Z	8
Radiation type	Cu *Kα*
μ (mm^{-1})	14.77
Crystal size (mm)	0.17 × 0.06 × 0.03
Data collection	
Diffractometer	Rigaku XtaLAB Synergy Dualflex diffractometer with a HyPix detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2023)
T_{min}, T_{max}	0.408, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38581, 5150, 3889
R_{int}	0.097
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.634
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.056, 0.156, 1.06
No. of reflections	5150
No. of parameters	365
No. of restraints	33
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.88, −0.78

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *CrystalMaker* (Palmer, 2020) and *OLEX2* (Dolomanov *et al.*, 2009).

Whilst the coordinated acetic acid molecule was clearly defined in the solution and subsequent refinement, peaks of residual electron density in the Fourier difference map were consistent with a second overlapping location for the acetic acid molecule. The peaks were assigned as acetic acid atoms and refined with complementary site occupancies. The result of the refinement showed two chemically similar positions for the coordinated acetic acid molecule (Fig. 1), with the occupancies for the major and minor positions refining to 86 and 14%, respectively. The carbonyl O atom was common to both orientations. For each of the positions of the acetic acid molecule, the hydroxyl group forms a hydrogen-bonding interaction with a neighbouring O atom of a coordinated acetate group [O15···O1 = 2.598 (6) Å and O15*A*···O12 = 2.62 (3) Å]. A peak of electron density (0.35 e Å^{-3}) was apparent between O15 and O1 (corresponding to the major orientation), and was consistent with the hydroxyl H atom. Hydroxyl H atoms were assigned, riding on O15 and O15*A*, with appropriate site occupancies. Details of the refinements can be found in the embedded instruction files in the CIF file.

3. Results and discussion

The combination of Fe$(NO_3)_3$, H_2hba and LiOAc in acetic anhydride yielded crystals of composition $Fe_3O(OAc)_7$(HOAc) (**1**). The structure consists of the common basic ferric acetate core in which three crystallographically distinct Fe^{III} centres

Table 2
Fe—O bond lengths (Å) in typical compounds containing an $[Fe_3O(OAc)_6(H_2O)_3]^+$ unit.

Compound	Individual Fe—μ_3-O(oxido) bond lengths	CSD refcode	Reference
$[Fe_3O(OAc)_6(H_2O)_3]NO_3{\cdot}2C_6H_{12}N_4{\cdot}5H_2O$	1.9034 (8), 1.9034 (8), 1.9057 (16)	EMAVAS	Balić *et al.* (2021)
$[Fe_3O(OAc)_6(H_2O)_3]NO_3{\cdot}C_2H_4O_2$	1.8961 (12), 1.8983 (11), 1.9120 (11)	GIZSEO03	Nieger (2016)
$[Fe_3O(OAc)_6(H_2O)_3]Cl{\cdot}6H_2O$	1.896 (4), 1.892 (4), 1.904 (4)	RIPLEH01	Shova *et al.* (1998)
$[Fe_3O(OAc)_6(H_2O)_3]ClO_4{\cdot}3H_2O$	1.8969 (12), 1.8965 (11), 1.9043 (13)	LINHEZ	Abánades Lázaro *et al.* (2023)

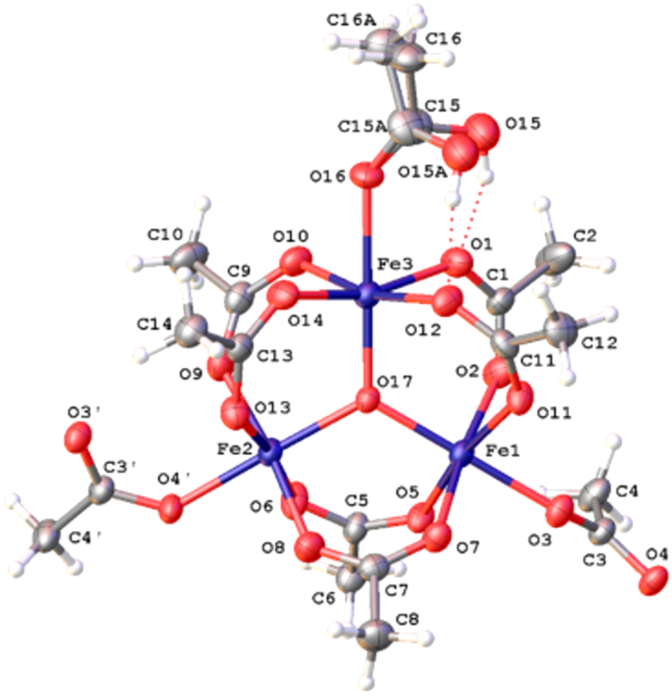


Figure 1
The structure of **1**, showing the disordered acetic acid group (top) with the atom-labelling scheme. The acetate group coordinated to Fe2 is also shown. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size. The red dotted lines represent hydrogen-bonding interactions.

bind to a central oxido dianion and six acetate ligands, each in a *syn–syn* conformation, spanning pairs of Fe^{III} centres, as indicated in Fig. 1. Whilst the $[Fe_3O(O_2CR)_6]^+$ unit (R = alkyl or aryl group) is a common fragment, the structure reported here is unique because of the ligands that are *trans* to the oxido group on each Fe centre. The *trans* sites on two of the Fe centres are occupied by bridging acetate anions which adopt a *syn–anti* configuration. These two anions are symmetry related to each other and result in the formation of a zigzag chain which extends parallel to the *a* direction, as indicated in Fig. 2. With the $[Fe_3O(OAc)_6]^+$ units bridged by a pair of acetate anions to symmetry-related counterparts, charge balance is achieved for this 1D coordination polymer.

Only a neutral ligand is required to complete the octahedral geometry on the remaining Fe centre. Ligands such as water could normally fulfil this role, but under anhydrous conditions, obtained using a solvent such as acetic anhydride, this is not possible. Remarkably, an acetic acid molecule coordinates to this Fe centre, as indicated in Figs. 1 and 2. The neutral molecule coordinates through a carbonyl O atom, while the hydroxyl group forms a geometrically favourable hydrogen bond with a coordinated O atom of a neighbouring acetate anion. The carbonyl bond distance (C15—O16) of 1.207 (7) Å is significantly shorter than the C—OH bond [C15—O15 = 1.329 (8) Å]. Whilst the difference in C—O bond distances is expected for an acetic acid molecule, it contrasts with the acetate anions, in which the C—O bonds have an intermediate bond length (~1.25 Å).

The $[Fe_3O(OAc)_6(H_2O)_3]^+$ fragment which is present in numerous crystal structures possesses a μ_3-oxido anion that forms Fe—O bonds of relatively similar length (see Table 2). In contrast, the three Fe—O(oxido) bond lengths in **1** show significant variation (Table 3), with the Fe—O bond (Fe3—O17) *trans* to the coordinated acetic acid being significantly shorter [1.872 (3) Å] than the other Fe—O bonds

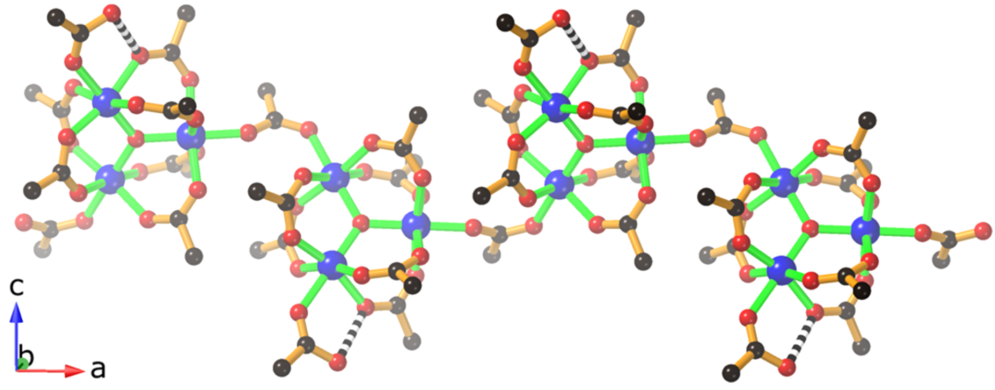


Figure 2
The polymeric structure of **1**, showing the zigzag chain extending in the *a* direction. C—O and C—C bonds are indicated by orange connections, Fe—O bonds by green connections and hydrogen bonds between the acetic acid hydroxyl O atoms and neighbouring acetate O atoms by striped connections. H atoms have been omitted for clarity.

Table 3
Fe—O(μ_3-oxido) bond lengths (Å) in **1**.

Bond	Bond length
Fe(bonded to acetic acid)—O(μ_3-oxido)	Fe3—O17 1.872 (3)
Fe(bonded only to acetate)—O(μ_3-oxido)	Fe1—O17 1.921 (3)
	Fe2—O17 1.940 (3)

which are *trans* to a bridging acetate anion [1.921 (3) and 1.940 (3) Å for Fe1—O17 and Fe2—O17, respectively]. This would appear to indicate a *trans* influence associated with the relatively weak coordination of the carbonyl O atom from the acetic acid molecule, which displays an Fe—O bond length of 2.144 (3) Å (Fe3—O16). In contrast, the bond lengths involving the acetate O atoms *trans* to O17 on Fe1 and Fe2 are 2.012 (3) and 2.014 (3) Å, respectively. Further distortion of the octahedral coordination geometry of Fe3 is apparent with the Fe centre lying 0.2585 (19) Å out of the plane of the acetate O atoms (O1, O10, O12 and O14) towards the μ_3-oxido atom (O17). In contrast, Fe1 and Fe2 lie only 0.1352 (17) and 0.1202 (19) Å, respectively, out of the plane of the corresponding acetate O atoms.

To the best of our knowledge, this is the first recorded example of the coordination of an acetic acid molecule to an Fe^{III} centre (CSD; Groom *et al.*, 2016). This is perhaps not surprising given that in its acid form, the Lewis basicity of acetic acid is expected to be very low. Its coordination in this present case may be attributed to the absence of solvent molecules that can serve as Lewis bases and the fact that the hydroxyl group of the acetic acid molecule is in an ideal position to form a relatively strong hydrogen bond with a neighbouring coordinated O atom [O15···O1 = 2.598 (6) Å and O15*A*···O12 = 2.62 (3) Å].

Although there are numerous potential O-atom acceptor sites for hydrogen bonding, the only O—H donor group, belonging to the acetic acid molecule, forms an intrachain hydrogen bond (O15···O1 or O15*A*···O12). As a result, there are only relatively weak intermolecular contacts between chains.

The structure of **1** is similar to that of $Mn_3O(OAc)_7(HOAc)$, which contains Mn^{III} centres, and adopts the same space group as $Fe_3O(OAc)_7(HOAc)$ [*Pbca*, *a* = 15.8661 (3), *b* = 15.864 (3) and *c* = 19.5003 (5) Å] and $Mn_3O(OAc)_7(HOAc)$ [*Pbca*, *a* = 16.07 (3), *b* = 19.84 (3) and *c* = 15.80 (2) Å] (Hessel & Romers, 1969). Despite the clear similarities in the general structure, there are some important differences associated with the high-spin d^4 configuration of the Mn^{III} centre which result in Jahn–Teller tetragonally distorted octahedral coordination environments for the three Mn^{III} centres. For each Mn centre, there are four short bonds to O atoms that form an approximate square plane and two longer Mn—O bonds that are *trans* to each other. In the case of the Mn^{III} centre coordinated by the acetic acid molecule, the two long bonds are the Mn—O(carbonyl) bond of the acetic acid molecule [2.33 (4) Å] and the Mn—μ_3-O bond [2.11 (4) Å]. For the remaining two Mn centres, the Mn—μ_3-O bonds are very short [1.85 (4) and 1.86 (4) Å], with the longer Mn—O bonds involving a pair of acetate O atoms that are *trans* to each other. The basicity of the oxido ligand would normally mean that it would form the shortest metal–oxygen bonds, but the poor basicity of the acetic acid ligand results in the Mn—O(carbonyl) bond and its *trans*-O atom (the μ_3-oxido ligand) being the long bonds in the tetragonally distorted octahedral environment.

A remarkable contrast in the electronic effect of the poorly coordinating acetic acid molecule is apparent in the schematic representation of the Fe and Mn structures presented in Fig. 3. Whereas the acetic acid molecule exerts a *trans* influence in the Fe structure, leading to a shortening of the Fe—μ_3-O bond, the effect of the acetic acid in the Mn structure is to cause the *trans* Mn—μ_3-O bond to become elongated.

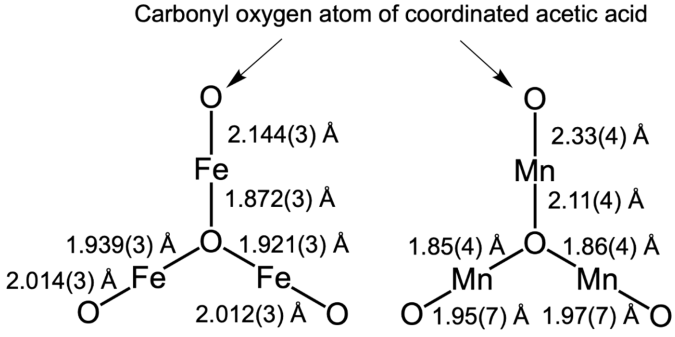


Figure 3
A schematic representation comparing selected metal–oxygen bond lengths in $Fe_3O(OAc)_7(HOAc)$ and $Mn_3O(OAc)_7(HOAc)$.

4. Conclusion

Compound **1** provides another example of a classic basic metal carboxylate structure, but unlike previous examples, the absence of common coordinating solvent molecules or neutral co-ligands results in the rare coordination of an acetic acid molecule to an Fe^{III} centre. Acetate ions provide a bridge between symmetry-related units, leading to the formation of a zigzag chain. A *trans* influence results in a short Fe—O bond opposite the acetic acid carbonyl O atom, which contrasts with the behaviour of the structurally similar compound, $Mn_3O(OAc)_7(HOAc)$, where a Jahn–Teller distortion results in the opposite effect, *i.e.* a lengthening of the Mn—O bond *trans* to the acetic acid.

Conflict of interest

The authors declare that there are no conflicts of interest.

Data availability

The data supporting the findings of this study are available within the article and its supplementary materials, and from the CSD.

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A polymeric form of basic iron(III) acetate with an acetic acid ligand

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Computing details

***catena*-Poly[hexa-μ-acetato-(acetic acid)-μ_3-oxido-*triangulo*-triiron(III)]-μ-acatato]**

Crystal data

$[Fe_3(C_2H_3O_2)_7O(C_2H_4O_2)]$
M_r = 656.91
Orthorhombic, *Pbca*
a = 15.8661 (3) Å
b = 15.8640 (3) Å
c = 19.5003 (5) Å
V = 4908.22 (18) Å^3
Z = 8
$F(000)$ = 2680
D_x = 1.778 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 8086 reflections
θ = 4.5–71.3°
μ = 14.77 mm^{-1}
T = 100 K
Irregular, clear red
0.17 × 0.06 × 0.03 mm

Data collection

Rigaku XtaLAB Synergy Dualflex diffractometer with a HyPix detector
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2023)
T_{min} = 0.408, T_{max} = 1.000
38581 measured reflections
5150 independent reflections
3889 reflections with $I > 2\sigma(I)$
R_{int} = 0.097
θ_{max} = 78.0°, θ_{min} = 4.5°
h = −19→19
k = −19→11
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.156
S = 1.06
5150 reflections
365 parameters
33 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2 + 9.0225P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Extinction correction: SHELXL2018 (Sheldrick, 2015*b*), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00020 (4)

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}	Occ. (<1)
Fe2	0.87313 (4)	0.56380 (4)	0.24593 (4)	0.02289 (19)	
Fe1	0.69003 (4)	0.58646 (4)	0.32908 (4)	0.02231 (19)	
Fe3	0.86841 (4)	0.65690 (4)	0.39570 (4)	0.0246 (2)	
O17	0.80980 (18)	0.60338 (18)	0.32468 (16)	0.0224 (6)	
O7	0.6692 (2)	0.6388 (2)	0.23676 (18)	0.0292 (7)	
O4	0.4361 (2)	0.5158 (2)	0.33477 (18)	0.0292 (7)	
O3	0.5648 (2)	0.5676 (2)	0.33395 (18)	0.0288 (7)	
O11	0.6673 (2)	0.70114 (19)	0.37278 (19)	0.0314 (8)	
O13	0.9305 (2)	0.67555 (19)	0.23243 (18)	0.0298 (8)	
O5	0.69210 (19)	0.47004 (19)	0.28768 (19)	0.0295 (7)	
O9	0.9673 (2)	0.5171 (2)	0.30472 (18)	0.0307 (8)	
O10	0.9534 (2)	0.5655 (2)	0.41216 (19)	0.0322 (8)	
O8	0.7843 (2)	0.6014 (2)	0.17790 (19)	0.0352 (8)	
O2	0.6976 (2)	0.5356 (2)	0.42557 (19)	0.0339 (8)	
O16	0.9358 (2)	0.7203 (2)	0.47589 (18)	0.0348 (8)	
O12	0.7907 (2)	0.7583 (2)	0.40255 (19)	0.0317 (8)	
O1	0.8000 (2)	0.6079 (2)	0.47643 (19)	0.0344 (8)	
O6	0.8212 (2)	0.4476 (2)	0.2477 (2)	0.0346 (8)	
O14	0.9501 (2)	0.7225 (2)	0.33875 (18)	0.0323 (8)	
C13	0.9627 (3)	0.7250 (3)	0.2750 (3)	0.0253 (9)	
O15	0.8500 (3)	0.7198 (3)	0.5652 (3)	0.0495 (14)	0.850 (8)
H15	0.821447	0.688590	0.539268	0.074*	0.850 (8)
C5	0.7475 (3)	0.4246 (3)	0.2606 (3)	0.0250 (9)	
C7	0.7123 (3)	0.6351 (3)	0.1831 (3)	0.0259 (10)	
C9	0.9860 (3)	0.5190 (3)	0.3674 (3)	0.0293 (10)	
C1	0.7361 (3)	0.5594 (3)	0.4776 (3)	0.0270 (10)	
C3	0.5125 (3)	0.5120 (3)	0.3514 (3)	0.0253 (9)	
C11	0.7128 (3)	0.7610 (3)	0.3938 (2)	0.0278 (10)	
C6	0.7230 (3)	0.3367 (3)	0.2417 (3)	0.0320 (11)	
H6A	0.682388	0.314990	0.275183	0.048*	
H6B	0.773259	0.300695	0.241520	0.048*	
H6C	0.697431	0.336593	0.195960	0.048*	
C4	0.5384 (3)	0.4397 (3)	0.3960 (3)	0.0336 (12)	
H4A	0.549084	0.460065	0.442612	0.050*	
H4B	0.589895	0.414139	0.377524	0.050*	
H4C	0.493312	0.397515	0.396934	0.050*	
C14	1.0197 (3)	0.7930 (3)	0.2485 (3)	0.0352 (12)	
H14A	1.053732	0.770803	0.210628	0.053*	
H14B	1.056951	0.812081	0.285465	0.053*	

H14C	0.985750	0.840483	0.232126	0.053*	
C12	0.6682 (4)	0.8427 (3)	0.4106 (3)	0.0382 (12)	
H12A	0.636010	0.861675	0.370641	0.057*	
H12B	0.710021	0.885706	0.422859	0.057*	
H12C	0.629890	0.833816	0.449360	0.057*	
C8	0.6745 (4)	0.6726 (4)	0.1193 (3)	0.0397 (13)	
H8A	0.657673	0.627291	0.088004	0.060*	
H8B	0.716247	0.708712	0.096733	0.060*	
H8C	0.624956	0.706268	0.131574	0.060*	
C10	1.0550 (4)	0.4610 (3)	0.3906 (3)	0.0423 (14)	
H10A	1.034602	0.402678	0.389846	0.063*	
H10B	1.072022	0.475906	0.437376	0.063*	
H10C	1.103467	0.466451	0.359779	0.063*	
C15	0.9169 (5)	0.7483 (4)	0.5314 (4)	0.0362 (19)	0.850 (8)
C2	0.7063 (4)	0.5301 (5)	0.5458 (3)	0.0504 (16)	
H2A	0.653924	0.559370	0.557694	0.076*	
H2B	0.749346	0.542475	0.580460	0.076*	
H2C	0.696120	0.469244	0.544262	0.076*	
C16	0.9628 (6)	0.8159 (5)	0.5663 (5)	0.041 (2)	0.850 (8)
H16A	1.012794	0.831020	0.539496	0.062*	0.850 (8)
H16B	0.980186	0.796539	0.611914	0.062*	0.850 (8)
H16C	0.926183	0.865299	0.570982	0.062*	0.850 (8)
C15A	0.926 (3)	0.771 (2)	0.5208 (16)	0.038 (6)	0.150 (8)
O15A	0.8598 (19)	0.821 (2)	0.5135 (18)	0.065 (5)	0.150 (8)
H15A	0.843372	0.819542	0.472593	0.097*	0.150 (8)
C16A	0.990 (3)	0.794 (3)	0.570 (3)	0.043 (9)	0.150 (8)
H16D	0.996531	0.748040	0.603652	0.064*	0.150 (8)
H16E	0.972879	0.845437	0.594350	0.064*	0.150 (8)
H16F	1.043516	0.803482	0.546737	0.064*	0.150 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe2	0.0191 (3)	0.0204 (3)	0.0292 (4)	−0.0017 (3)	0.0015 (3)	−0.0018 (3)
Fe1	0.0189 (3)	0.0191 (3)	0.0290 (4)	0.0005 (3)	0.0002 (3)	−0.0002 (3)
Fe3	0.0220 (4)	0.0230 (4)	0.0288 (4)	−0.0008 (3)	−0.0007 (3)	−0.0013 (3)
O17	0.0196 (15)	0.0203 (14)	0.0272 (17)	0.0004 (12)	0.0008 (13)	−0.0011 (12)
O7	0.0255 (17)	0.0307 (17)	0.0315 (19)	−0.0002 (13)	−0.0009 (14)	0.0059 (14)
O4	0.0201 (16)	0.0346 (17)	0.0328 (19)	−0.0019 (13)	−0.0035 (14)	0.0079 (14)
O3	0.0226 (16)	0.0248 (15)	0.039 (2)	0.0024 (13)	−0.0004 (14)	0.0030 (14)
O11	0.0258 (17)	0.0249 (16)	0.043 (2)	−0.0016 (13)	0.0060 (15)	−0.0087 (15)
O13	0.0314 (18)	0.0217 (15)	0.036 (2)	−0.0021 (13)	0.0059 (15)	−0.0027 (13)
O5	0.0227 (16)	0.0236 (15)	0.042 (2)	−0.0023 (13)	0.0002 (15)	−0.0112 (14)
O9	0.0257 (17)	0.0348 (18)	0.0317 (19)	0.0055 (14)	0.0016 (14)	0.0003 (15)
O10	0.0289 (18)	0.0302 (17)	0.038 (2)	0.0060 (14)	−0.0074 (15)	−0.0021 (15)
O8	0.0291 (18)	0.041 (2)	0.035 (2)	0.0066 (15)	−0.0031 (15)	−0.0037 (16)
O2	0.0312 (19)	0.0387 (19)	0.0319 (19)	−0.0089 (15)	−0.0003 (15)	0.0091 (15)
O16	0.037 (2)	0.0362 (19)	0.0316 (19)	−0.0045 (15)	−0.0047 (16)	−0.0113 (16)

O12	0.0285 (18)	0.0244 (16)	0.042 (2)	0.0044 (13)	−0.0041 (15)	−0.0062 (14)
O1	0.0339 (19)	0.0403 (19)	0.0289 (18)	−0.0093 (15)	0.0007 (15)	0.0015 (15)
O6	0.0275 (18)	0.0236 (16)	0.053 (2)	−0.0048 (14)	0.0095 (16)	−0.0080 (15)
O14	0.0310 (18)	0.0332 (17)	0.0326 (19)	−0.0112 (14)	−0.0005 (15)	−0.0008 (15)
C13	0.022 (2)	0.022 (2)	0.032 (3)	0.0028 (17)	−0.0008 (19)	−0.0006 (18)
O15	0.046 (3)	0.055 (3)	0.047 (3)	−0.011 (2)	0.006 (2)	−0.009 (2)
C5	0.020 (2)	0.020 (2)	0.035 (3)	−0.0013 (17)	0.0028 (19)	0.0008 (18)
C7	0.029 (2)	0.017 (2)	0.031 (3)	0.0007 (17)	−0.004 (2)	−0.0014 (17)
C9	0.026 (2)	0.018 (2)	0.044 (3)	0.0015 (17)	0.000 (2)	0.000 (2)
C1	0.021 (2)	0.029 (2)	0.031 (3)	−0.0005 (18)	−0.003 (2)	0.0018 (19)
C3	0.020 (2)	0.025 (2)	0.031 (2)	−0.0039 (17)	−0.0010 (19)	−0.0004 (18)
C11	0.035 (3)	0.023 (2)	0.025 (2)	−0.0001 (19)	0.005 (2)	−0.0026 (18)
C6	0.028 (2)	0.021 (2)	0.047 (3)	−0.0010 (19)	−0.001 (2)	−0.004 (2)
C4	0.023 (2)	0.031 (2)	0.046 (3)	−0.0057 (19)	−0.004 (2)	0.010 (2)
C14	0.032 (3)	0.028 (2)	0.045 (3)	−0.005 (2)	−0.001 (2)	0.000 (2)
C12	0.043 (3)	0.027 (2)	0.045 (3)	0.009 (2)	0.000 (3)	−0.005 (2)
C8	0.042 (3)	0.040 (3)	0.036 (3)	0.003 (2)	−0.008 (2)	0.004 (2)
C10	0.036 (3)	0.036 (3)	0.055 (4)	0.009 (2)	−0.015 (3)	−0.004 (2)
C15	0.041 (4)	0.024 (4)	0.043 (4)	0.003 (3)	0.000 (3)	0.002 (3)
C2	0.040 (3)	0.075 (4)	0.035 (3)	−0.022 (3)	−0.005 (3)	0.019 (3)
C16	0.045 (5)	0.039 (5)	0.040 (4)	−0.008 (4)	−0.007 (4)	−0.008 (4)
C15A	0.049 (9)	0.017 (11)	0.047 (10)	−0.001 (9)	0.004 (9)	−0.001 (10)
O15A	0.057 (9)	0.069 (9)	0.068 (10)	0.003 (8)	−0.001 (9)	−0.015 (9)
C16A	0.058 (18)	0.026 (17)	0.046 (15)	0.003 (15)	−0.006 (15)	0.004 (14)

Geometric parameters (Å, º)

Fe2—O17	1.940 (3)	C5—C6	1.494 (6)
Fe2—O4^{i}	2.014 (3)	C7—C8	1.504 (7)
Fe2—O13	2.010 (3)	C9—C10	1.500 (7)
Fe2—O9	2.023 (3)	C1—C2	1.485 (7)
Fe2—O8	2.026 (4)	C3—C4	1.496 (7)
Fe2—O6	2.020 (3)	C11—C12	1.513 (7)
Fe1—O17	1.921 (3)	C6—H6A	0.9800
Fe1—O7	2.010 (3)	C6—H6B	0.9800
Fe1—O3	2.012 (3)	C6—H6C	0.9800
Fe1—O11	2.041 (3)	C4—H4A	0.9800
Fe1—O5	2.016 (3)	C4—H4B	0.9800
Fe1—O2	2.051 (4)	C4—H4C	0.9800
Fe3—O17	1.872 (3)	C14—H14A	0.9800
Fe3—O10	2.006 (3)	C14—H14B	0.9800
Fe3—O16	2.144 (3)	C14—H14C	0.9800
Fe3—O12	2.030 (3)	C12—H12A	0.9800
Fe3—O1	2.064 (4)	C12—H12B	0.9800
Fe3—O14	1.999 (3)	C12—H12C	0.9800
O7—C7	1.252 (6)	C8—H8A	0.9800
O4—C3	1.256 (6)	C8—H8B	0.9800
O3—C3	1.258 (5)	C8—H8C	0.9800

O11—C11	1.261 (6)	C10—H10A	0.9800
O13—C13	1.250 (6)	C10—H10B	0.9800
O5—C5	1.253 (5)	C10—H10C	0.9800
O9—C9	1.259 (6)	C15—C16	1.464 (9)
O10—C9	1.254 (6)	C2—H2A	0.9800
O8—C7	1.265 (6)	C2—H2B	0.9800
O2—C1	1.243 (6)	C2—H2C	0.9800
O16—C15	1.207 (7)	C16—H16A	0.9800
O16—C15A	1.201 (12)	C16—H16B	0.9800
O12—C11	1.250 (6)	C16—H16C	0.9800
O1—C1	1.272 (6)	C15A—O15A	1.320 (19)
O6—C5	1.252 (5)	C15A—C16A	1.45 (2)
O14—C13	1.261 (6)	O15A—H15A	0.8400
C13—C14	1.500 (7)	C16A—H16D	0.9800
O15—H15	0.8400	C16A—H16E	0.9800
O15—C15	1.329 (8)	C16A—H16F	0.9800

O17—Fe2—O4^{i}	176.57 (13)	O9—C9—C10	116.8 (5)
O17—Fe2—O13	93.02 (13)	O10—C9—O9	126.3 (4)
O17—Fe2—O9	93.01 (13)	O10—C9—C10	116.9 (5)
O17—Fe2—O8	93.58 (14)	O2—C1—O1	124.0 (5)
O17—Fe2—O6	94.07 (14)	O2—C1—C2	118.7 (4)
O4^{i}—Fe2—O9	86.44 (14)	O1—C1—C2	117.3 (5)
O4^{i}—Fe2—O8	86.85 (14)	O4—C3—O3	122.2 (4)
O4^{i}—Fe2—O6	82.53 (14)	O4—C3—C4	116.9 (4)
O13—Fe2—O4^{i}	90.39 (14)	O3—C3—C4	120.9 (4)
O13—Fe2—O9	93.62 (14)	O11—C11—C12	116.7 (5)
O13—Fe2—O8	88.24 (15)	O12—C11—O11	125.8 (4)
O13—Fe2—O6	172.74 (15)	O12—C11—C12	117.5 (4)
O9—Fe2—O8	173.05 (15)	C5—C6—H6A	109.5
O6—Fe2—O9	87.54 (15)	C5—C6—H6B	109.5
O6—Fe2—O8	89.79 (15)	C5—C6—H6C	109.5
O17—Fe1—O7	93.73 (14)	H6A—C6—H6B	109.5
O17—Fe1—O3	179.44 (13)	H6A—C6—H6C	109.5
O17—Fe1—O11	93.97 (13)	H6B—C6—H6C	109.5
O17—Fe1—O5	95.39 (13)	C3—C4—H4A	109.5
O17—Fe1—O2	92.17 (13)	C3—C4—H4B	109.5
O7—Fe1—O3	86.63 (14)	C3—C4—H4C	109.5
O7—Fe1—O11	88.66 (15)	H4A—C4—H4B	109.5
O7—Fe1—O5	91.29 (14)	H4A—C4—H4C	109.5
O7—Fe1—O2	173.71 (14)	H4B—C4—H4C	109.5
O3—Fe1—O11	86.47 (13)	C13—C14—H14A	109.5
O3—Fe1—O5	84.17 (13)	C13—C14—H14B	109.5
O3—Fe1—O2	87.49 (14)	C13—C14—H14C	109.5
O11—Fe1—O2	88.75 (15)	H14A—C14—H14B	109.5
O5—Fe1—O11	170.63 (13)	H14A—C14—H14C	109.5
O5—Fe1—O2	90.34 (15)	H14B—C14—H14C	109.5
O17—Fe3—O10	97.15 (14)	C11—C12—H12A	109.5

O17—Fe3—O16	178.92 (14)	C11—C12—H12B	109.5
O17—Fe3—O12	96.11 (14)	C11—C12—H12C	109.5
O17—Fe3—O1	97.59 (14)	H12A—C12—H12B	109.5
O17—Fe3—O14	98.45 (14)	H12A—C12—H12C	109.5
O10—Fe3—O16	83.53 (14)	H12B—C12—H12C	109.5
O10—Fe3—O12	165.93 (15)	C7—C8—H8A	109.5
O10—Fe3—O1	87.65 (15)	C7—C8—H8B	109.5
O12—Fe3—O16	83.28 (14)	C7—C8—H8C	109.5
O12—Fe3—O1	85.95 (15)	H8A—C8—H8B	109.5
O1—Fe3—O16	83.27 (14)	H8A—C8—H8C	109.5
O14—Fe3—O10	91.69 (15)	H8B—C8—H8C	109.5
O14—Fe3—O16	80.68 (14)	C9—C10—H10A	109.5
O14—Fe3—O12	91.01 (15)	C9—C10—H10B	109.5
O14—Fe3—O1	163.90 (14)	C9—C10—H10C	109.5
Fe1—O17—Fe2	120.18 (16)	H10A—C10—H10B	109.5
Fe3—O17—Fe2	118.37 (15)	H10A—C10—H10C	109.5
Fe3—O17—Fe1	121.44 (16)	H10B—C10—H10C	109.5
C7—O7—Fe1	129.8 (3)	O16—C15—O15	121.1 (6)
C3—O4—Fe2^{ii}	134.3 (3)	O16—C15—C16	124.3 (7)
C3—O3—Fe1	140.3 (3)	O15—C15—C16	114.6 (6)
C11—O11—Fe1	134.9 (3)	C1—C2—H2A	109.5
C13—O13—Fe2	130.6 (3)	C1—C2—H2B	109.5
C5—O5—Fe1	135.0 (3)	C1—C2—H2C	109.5
C9—O9—Fe2	135.7 (3)	H2A—C2—H2B	109.5
C9—O10—Fe3	126.2 (3)	H2A—C2—H2C	109.5
C7—O8—Fe2	134.5 (3)	H2B—C2—H2C	109.5
C1—O2—Fe1	131.2 (3)	C15—C16—H16A	109.5
C15—O16—Fe3	134.6 (4)	C15—C16—H16B	109.5
C15A—O16—Fe3	141.4 (18)	C15—C16—H16C	109.5
C11—O12—Fe3	128.3 (3)	H16A—C16—H16B	109.5
C1—O1—Fe3	131.3 (3)	H16A—C16—H16C	109.5
C5—O6—Fe2	130.6 (3)	H16B—C16—H16C	109.5
C13—O14—Fe3	131.9 (3)	O16—C15A—O15A	115 (3)
O13—C13—O14	124.8 (4)	O16—C15A—C16A	124 (3)
O13—C13—C14	118.0 (5)	O15A—C15A—C16A	119 (2)
O14—C13—C14	117.2 (4)	C15A—O15A—H15A	109.5
C15—O15—H15	109.5	C15A—C16A—H16D	109.5
O5—C5—C6	117.4 (4)	C15A—C16A—H16E	109.5
O6—C5—O5	125.0 (4)	C15A—C16A—H16F	109.5
O6—C5—C6	117.7 (4)	H16D—C16A—H16E	109.5
O7—C7—O8	125.5 (5)	H16D—C16A—H16F	109.5
O7—C7—C8	117.1 (4)	H16E—C16A—H16F	109.5
O8—C7—C8	117.4 (5)		

Fe2^{ii}—O4—C3—O3	30.4 (7)	Fe3—O10—C9—O9	−5.2 (7)
Fe2^{ii}—O4—C3—C4	−152.1 (4)	Fe3—O10—C9—C10	173.7 (3)
Fe2—O13—C13—O14	−15.8 (7)	Fe3—O16—C15—O15	23.5 (11)
Fe2—O13—C13—C14	164.9 (3)	Fe3—O16—C15—C16	−155.5 (6)

Fe2—O9—C9—O10	−12.1 (8)	Fe3—O16—C15A—O15A	−21 (7)
Fe2—O9—C9—C10	168.9 (4)	Fe3—O16—C15A—C16A	175 (3)
Fe2—O8—C7—O7	−15.6 (7)	Fe3—O12—C11—O11	−6.6 (8)
Fe2—O8—C7—C8	165.4 (4)	Fe3—O12—C11—C12	172.5 (4)
Fe2—O6—C5—O5	−13.5 (8)	Fe3—O1—C1—O2	−5.0 (7)
Fe2—O6—C5—C6	165.7 (4)	Fe3—O1—C1—C2	175.0 (4)
Fe1—O7—C7—O8	−6.2 (7)	Fe3—O14—C13—O13	−9.6 (7)
Fe1—O7—C7—C8	172.7 (3)	Fe3—O14—C13—C14	169.7 (3)
Fe1—O3—C3—O4	−165.5 (4)	O10—Fe3—O17—Fe2	−53.88 (19)
Fe1—O3—C3—C4	17.1 (8)	O10—Fe3—O17—Fe1	125.52 (19)
Fe1—O11—C11—O12	−12.3 (8)	O12—Fe3—O17—Fe2	130.85 (18)
Fe1—O11—C11—C12	168.5 (4)	O12—Fe3—O17—Fe1	−49.8 (2)
Fe1—O5—C5—O6	−6.2 (8)	O1—Fe3—O17—Fe2	−142.44 (17)
Fe1—O5—C5—C6	174.6 (4)	O1—Fe3—O17—Fe1	37.0 (2)
Fe1—O2—C1—O1	−22.6 (7)	O14—Fe3—O17—Fe2	38.91 (19)
Fe1—O2—C1—C2	157.4 (4)	O14—Fe3—O17—Fe1	−141.69 (18)

Symmetry codes: (i) $x+1/2, y, -z+1/2$; (ii) $x-1/2, y, -z+1/2$.