

## Bis(1-ferrocenylbutane-1,3-dionato- $\kappa^2O,O'$ )copper(II) and bis(1,3-diferrocenylpropane-1,3-dionato- $\kappa^2O,O'$ )copper(II)

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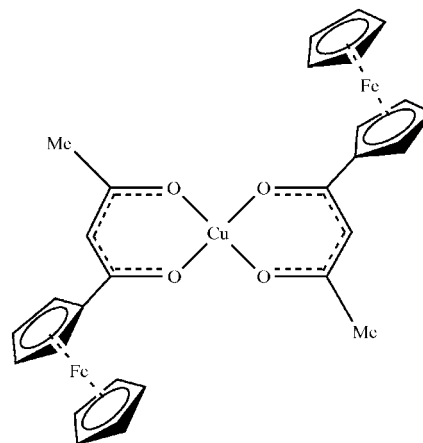
The title compounds,  $[\text{CuFe}_2(\text{C}_5\text{H}_5)_2(\text{C}_9\text{H}_8\text{O}_2)_2]$ , (I), and  $[\text{CuFe}_4(\text{C}_5\text{H}_5)_4(\text{C}_{13}\text{H}_9\text{O}_2)_2]$ , (II), are four-coordinate square-planar copper(II) complexes with two bidentate 1-ferrocenylbutane-1,3-dionate or 1,3-diferrocenylpropane-1,3-dionate ligands, respectively. The copper ion in (I) lies on an inversion centre, with one-half of the molecule in the asymmetric unit, while in (II), there are two independent half molecules in the asymmetric unit, with the copper ions also situated on inversion centres. The ferrocene substituents in (I) are in an *anti* arrangement. The molecules assemble in the crystal structure in layers with ferrocene groups at the surface. The pairs of ferrocene substituents on each ligand in complex (II) are *syn* and these adopt an *anti* arrangement with respect to the pair on the other diketonate ligand. As found in (I), complexes assemble in a layered structure with ferrocene-coated surfaces.

### Comment

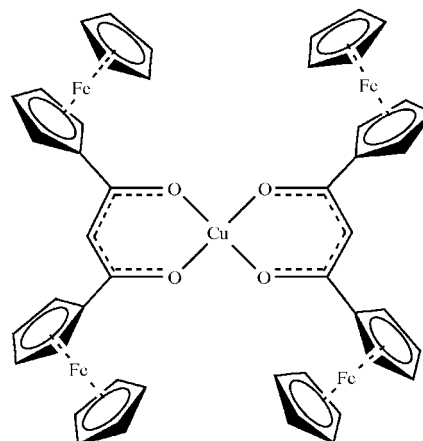
The 1,3- $\beta$ -diketones 1-ferrocenylbutane-1,3-dione ( $\text{HL}_1$ ;  $\text{FcCOCH}_2\text{COCH}_3$ ; Cain *et al.* 1961; Hennig & Gurtler, 1968; Bell *et al.*, 1992; Zakaria *et al.*, 1995) and 1,3-diferrocenylpropane-1,3-dione ( $\text{HL}_2$ ;  $\text{FcCOCH}_2\text{COFc}$ ; Woisetschlager *et al.*, 1999; du Plessis *et al.*, 1998, 2001) form coordination (Zanello *et al.*, 1998; Che *et al.*, 1998; Li *et al.*, 2002) and organometallic complexes of interest in catalysis (Abiko & Wang, 1996, 1998; Cullen *et al.*, 1991; Swarts *et al.*, 1993; Woisetschlager *et al.*, 2000; Vosloo *et al.*, 2002; Conradie *et al.*, 2005).

Copper(II) complexes of these ligands, *viz.* the title compounds  $\text{Cu}(\text{L}_1)_2$ , (I), and  $\text{Cu}(\text{L}_2)_2$ , (II), are readily formed upon mixing of methanol solutions of copper acetate and methanol solutions of either  $\text{HL}_1$  or  $\text{HL}_2$ . These complexes have been used in the purification of the ligands (Imai & Ota, 1974; Zanello *et al.*, 1998; du Plessis *et al.*, 1998). Compound (I) has been further characterized by elemental analysis and cyclic voltammetry (Zanello *et al.*, 1998). Related complexes,

namely bis(1-ethoxycarbonyl-3-ferrocenyl-propane-1,3-dionato)copper(II), (III), and bis[1,3-bis(2-methylferrocenyl)-propane-1,3-dionato]copper(II), have been prepared and characterized (Prokop *et al.*, 1999, 2001; Abiko & Wang, 1998).



(I)

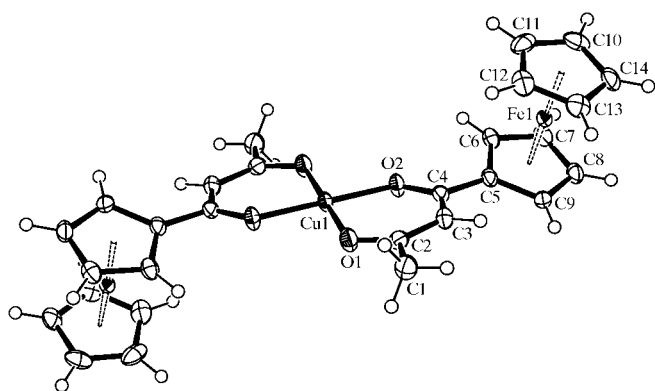


(II)

The molecular structure of (I) is shown in Fig. 1. The four-coordinate copper ion lies on a crystallographic inversion centre, leading to a near square-planar  $\text{CuO}_4$  unit (Table 1). The mean planes of the two butanedionate ligands ( $\text{O1/C2-C4/O2}$ , with an r.m.s. deviation of  $0.018 \text{ \AA}$ ) are *anti* with respect to the  $\text{CuO}_4$  plane, with tilt angles of  $7.80 (9)^\circ$ . The two ferrocene groups are *anti* in the complex, with the C5–C9 cyclopentadienyl ring rotated by  $26.7 (1)^\circ$  with respect to the  $\text{O1/C2-C4/O2}$  ligand plane. This arrangement differs from that of complex (III), in which the ferrocenyl groups are *syn* (Prokop *et al.*, 1999), whilst in the aqua complex of (III), they are *anti* (Prokop *et al.*, 2001). The cyclopentadienyl rings are in an eclipsed arrangement within each ferrocene group, with pseudo-torsion angles  $\text{C} \cdots \text{Cg1} \cdots \text{Cg2} \cdots \text{C}$  ranging from  $0.79$  to  $1.39^\circ$  (Cg1 and Cg2 are the centroids of the C5–C9 and C10–C14 cyclopentadienyl rings). The  $\text{Fe} \cdots \text{Cg1}$  and  $\text{Fe} \cdots \text{Cg2}$  distances are  $1.651 (1)$  and  $1.655 (1) \text{ \AA}$ , respectively, with a  $\text{Cg1} \cdots \text{Fe} \cdots \text{Cg2}$  angle of  $179.0^\circ$ .

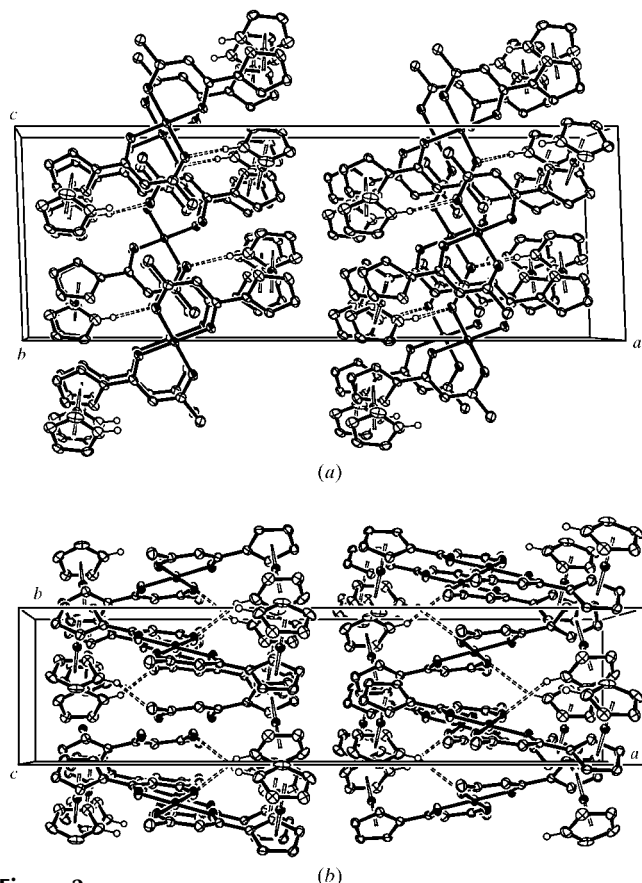
The molecules in the crystal structure of (I) assemble in layers aligned with the *bc* plane. The copper  $\beta$ -diketonate units are stacked along the *b* axis ( $\text{Cu} \cdots \text{Cu} = 7.413 \text{ \AA}$ ), with

methyl groups from complexes in adjacent stacks interleaved between them (Fig. 2). There are C—H... $\pi$  contacts between ferrocene groups [C13—H13...Cg1<sup>i</sup> = 2.94 Å and C6—H6...Cg2<sup>ii</sup> = 3.10 Å; symmetry codes: (i)  $x, -y, z - \frac{1}{2}$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ] on the surface of the layers. Each ferrocene group on the surface adopts a near orthogonal arrangement with respect to a ferrocene ring on a neighbouring layer [Fe...Fe<sup>iii</sup> = 5.4373 (4) Å; symmetry code: (iii)  $-x, y, -z + \frac{1}{2}$ ].



**Figure 1**

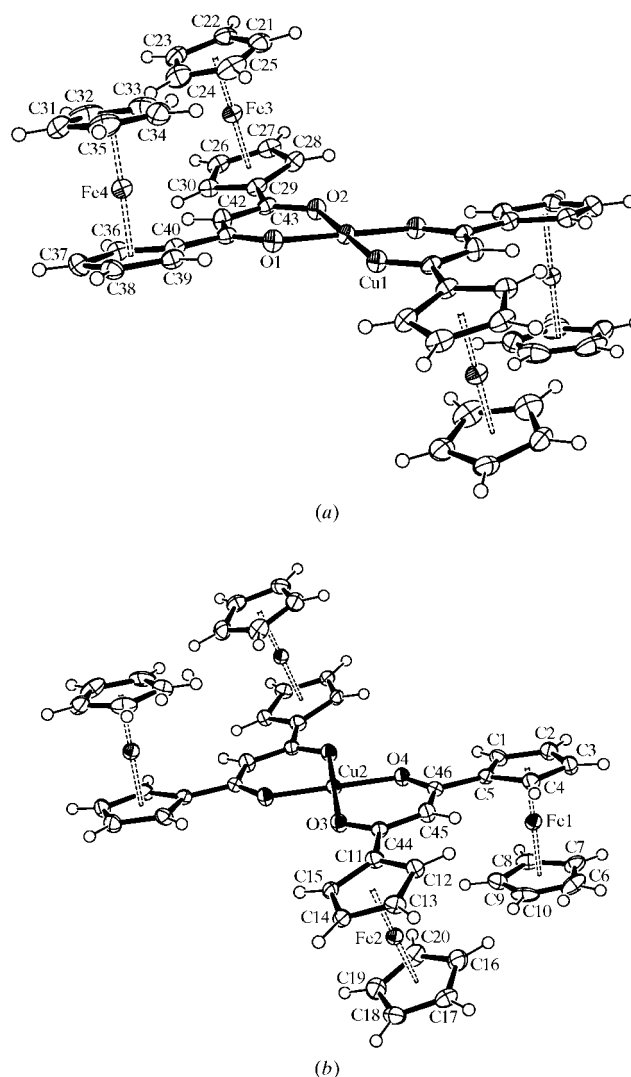
The structure of (I), showing 50% probability displacement ellipsoids for non-H atoms. Unlabelled atoms are related to labelled atoms by the symmetry code  $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ .



**Figure 2**

The arrangement of complex (I) in the crystal, viewed (a) along the *b* axis and (b) along the *c* axis.

The molecular structure of (II) is shown in Fig. 3. The asymmetric unit consists of two independent half molecules of bis(1,3-diferrocenyl-1,3-propanedionato)copper(II) with the copper ions situated on crystallographic inversion centres, again leading to two near square-planar CuO<sub>4</sub> units (Table 2). The two propanedionate ligand planes are tilted in an *anti* arrangement, with tilt angles of the two ligand planes (O1/C41–C43/O2, with an r.m.s. deviation of 0.016 Å, and O3/C44–C46/O4, with an r.m.s. deviation of 0.012 Å) of 6.5 (2) and 5.3 (2)° with respect to the Cu1O<sub>4</sub> and Cu2O<sub>4</sub> planes, respectively. Within each copper complex, the two ferrocene groups on each propanedionate ligand are in a *syn* arrangement and these are *anti* to the two ferrocene substituents on the other ligand (Fig. 3). The cyclopentadienyl rings on the ferrocene groups attached to the Cu1 complex are in a near eclipsed arrangement, with average pseudo-torsion angles



**Figure 3**

The structure of (II), showing 50% probability displacement ellipsoids for non-H atoms in (a) the Cu1 complex and (b) the Cu2 complex. Unlabelled atoms are related to labelled atoms by the symmetry code  $(1 - x, 1 - y, 1 - z)$  for the Cu1 complex and by  $(1 - x, -y, -z)$  for the Cu2 complex.

$C \cdots Cg3 \cdots Cg4 \cdots C$  for ferrocene Fe3 and Fe4 of 13.3 and 14.3°, respectively (Cg3 and Cg4 are the centroids of either the Fe3 C21–C25 and C26–C30 or the Fe4 C31–C35 and C36–C40 cyclopentadienyl rings). The Fe3···Cg and Fe4···Cg distances are 1.662 (2) and 1.652 (2) Å, respectively, for Cg3, and 1.656 (2) and 1.649 (2) Å for Cg4, with Cg3···Fe···Cg4 angles of 179.7 and 178.2°. A ferrocene group, Fe1, attached to the Cu2 complex contains a disordered cyclopentadienyl ring in either a near staggered (major component, atoms C1–C5; average pseudo-torsion angle  $C \cdots Cg5 \cdots Cg6 \cdots C = 25.5^\circ$ ; Cg5 and Cg6 are the centroids of either the Fe3 C1–C5 and C6–C10 or the Fe4 C11–C15 and C16–C20 cyclopentadienyl rings) or a near eclipsed arrangement (minor component, atoms C47–C51; average pseudo-torsion angles  $C \cdots Cg5 \cdots Cg6 \cdots C =$

$7.0^\circ$ ), whilst those on Fe2 are eclipsed (average pseudo-torsion angles  $C \cdots Cg5 \cdots Cg6 \cdots C = 7.5^\circ$ ). The Fe1···Cg and Fe2···Cg distances are 1.653 (2) and 1.649 (2) Å, respectively, for Cg5, and 1.680 (5) and 1.655 (2) Å for Cg6, with Cg5···Fe···Cg6 angles of 179.8 and 179.5°. The ferrocene groups are slightly tilted with respect to the propanedionate ligand mean planes [ $14.9 (1)^\circ$  for the C26–C30 ring and  $8.1 (2)^\circ$  for the C36–C40 ring with respect to the O12/C41–C43 plane, and  $13.4 (1)^\circ$  for the C11–C15 ring and  $6.8 (2)^\circ$  for the C1–C5 ring with respect to the O3/O4/C44–C46 plane].

The copper complexes assemble in the crystal structure of (II) *via* ferrocene  $C-H \cdots O$  and  $C-H \cdots \pi$  interactions (Table 3). Four complexes are arranged in a rectangular arrangement of four pairs of ferrocene groups (Fig. 4*a*). Within this arrangement is a  $44 \text{ \AA}^3$  solvent-accessible void with no residual electron density (PLATON; Spek, 2003). These arrangements continue in the *bc* plane, giving a layered structure with interdigitated ferrocene groups on the surfaces of each layer (Fig. 4*b*).

## Experimental

Complex (I) was prepared by mixing a warm solution of HL<sub>1</sub> (500 mg, 1.85 mmol, in 20 ml methanol) with a warm solution of copper(II) acetate dihydrate (176 mg, 0.88 mmol, in 20 ml methanol). A brown–gold precipitate formed which was filtered off, washed with methanol and dried to give 482 mg of (I) (91% yield). Red crystals of (I) were grown by vapour diffusion of ethanol into a benzene solution. Complex (II) was prepared by mixing a warm solution of HL<sub>2</sub> (371 mg, 0.84 mmol, in 20 ml methanol) with a warm solution of copper(II) acetate dihydrate (84 mg, 0.42 mmol, in 20 ml methanol). The solution was refluxed for 30 min, cooled to room temperature, filtered and washed with ethyl acetate to give 182 mg of a red crystalline precipitate (46% yield). Red crystals of (II) were grown by vapour diffusion of hexane into a benzene solution.

## Compound (I)

### Crystal data

[CuFe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 601.73  
 Monoclinic, *C*2/*c*  
*a* = 29.6410 (3) Å  
*b* = 7.4132 (1) Å  
*c* = 10.5656 (2) Å  
 $\beta$  = 92.1086 (9)°  
*V* = 2320.06 (6) Å<sup>3</sup>

*Z* = 4  
*D<sub>x</sub>* = 1.723 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 $\mu$  = 2.18 mm<sup>−1</sup>  
*T* = 203 (2) K  
 Plate, red  
 0.38 × 0.28 × 0.03 mm

### Data collection

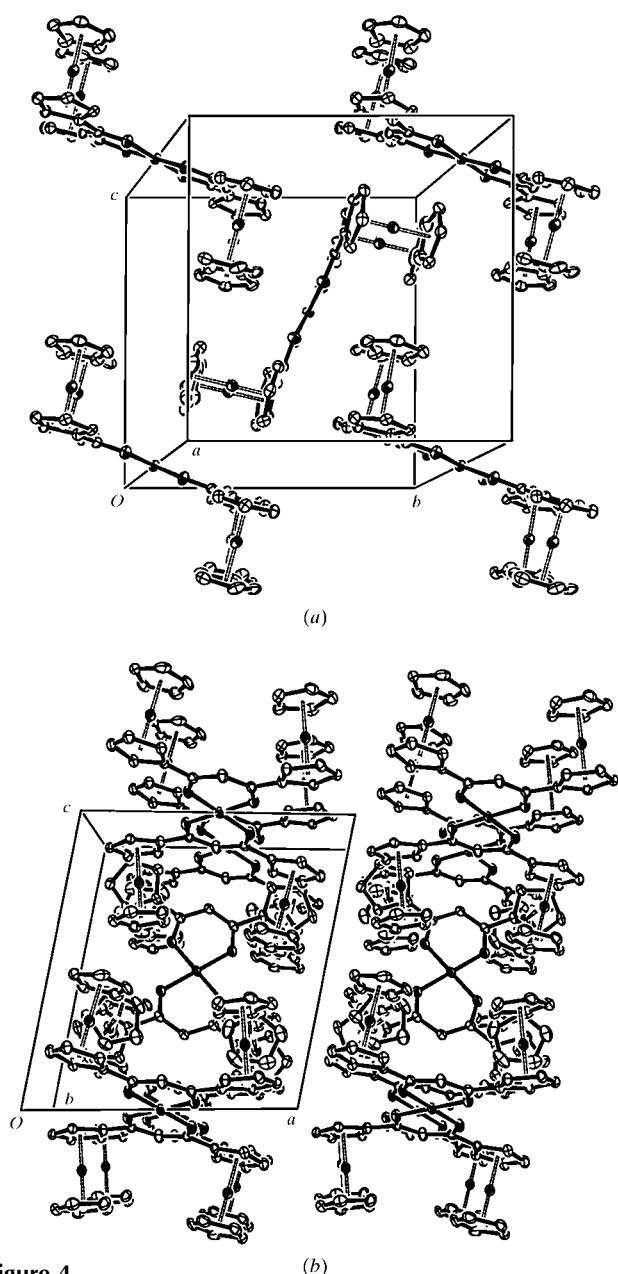
Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
*T<sub>min</sub>* = 0.655, *T<sub>max</sub>* = 0.952

7126 measured reflections  
 2558 independent reflections  
 2195 reflections with  $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.021  
 $\theta_{\text{max}}$  = 27.5°

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.100$   
*S* = 1.21  
 2558 reflections  
 161 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 1.6252P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.69 \text{ e \AA}^{-3}$



**Figure 4**  
 The arrangement of complex (II) in the crystal, viewed (*a*) along the *a* axis and (*b*) along the *b* axis.

**Table 1**

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

Cu1—O1	1.9033 (18)	O2—C4	1.285 (3)
Cu1—O2	1.9182 (16)	C2—C3	1.395 (3)
O1—C2	1.280 (3)	C3—C4	1.396 (3)
O1—Cu1—O2	93.91 (7)	O1—Cu1—O2 <sup>i</sup>	86.09 (7)

Symmetry code: (i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .**Compound (II)***Crystal data*

[CuFe <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> ) <sub>4</sub> (C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub> ]	$V = 1892.49 (4) \text{ \AA}^3$
$M_r = 941.70$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.653 \text{ Mg m}^{-3}$
$a = 11.9182 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 12.8881 (1) \text{ \AA}$	$\mu = 2.10 \text{ mm}^{-1}$
$c = 12.9097 (1) \text{ \AA}$	$T = 200 (2) \text{ K}$
$\alpha = 89.6701 (4)^\circ$	Prism, brown
$\beta = 78.6174 (4)^\circ$	$0.16 \times 0.14 \times 0.1 \text{ mm}$
$\gamma = 76.987 (8)^\circ$	

*Data collection*

Siemens SMART CCD area-detector diffractometer	17654 measured reflections
$\omega$ scans	7556 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	5859 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.650, T_{\max} = 0.803$	$R_{\text{int}} = 0.038$
	$\theta_{\max} = 26.4^\circ$

*Refinement*

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.6255P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.07$	$\Delta\rho_{\max} = 0.95 \text{ e \AA}^{-3}$
7556 reflections	$\Delta\rho_{\min} = -1.23 \text{ e \AA}^{-3}$
545 parameters	
H-atom parameters constrained	

**Table 2**

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

Cu1—O1	1.911 (3)	Cu2—O4	1.912 (2)
Cu1—O2	1.919 (2)	Cu2—O3	1.926 (3)
O1 <sup>i</sup> —Cu1—O2	86.68 (11)	O4 <sup>ii</sup> —Cu2—O3	86.38 (10)
O1—Cu1—O2	93.32 (11)	O4—Cu2—O3	93.62 (10)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y, -z$ .**Table 3**C—H...O and C—H... $\pi$  contacts in (II) (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C19—H...Cg <sup>a</sup>	0.93	2.77	3.63	154
C49—H...Cg <sup>b</sup>	0.93	2.84	3.71	155
C9—H...Cg <sup>b</sup>	0.93	2.98	3.68	134
C34—H...Cg <sup>c</sup>	0.93	2.63	3.55	170
C21—H...Cg <sup>d</sup>	0.93	3.15	3.82	130
C17—H...O1 <sup>e</sup>	0.93	2.73	3.30	121
C51—H...O2 <sup>e</sup>	0.93	2.41	3.26	153
C32—H...O4 <sup>f</sup>	0.93	2.55	3.45	163

Notes: (a) Cg is the centroid of ring C31–C35 at (x, y, z); (b) Cg is the centroid of ring C21–C25 at (x, y, z); (c) Cg is the centroid of ring C6–C10 at (1 – x, –y, 1 – z); (d) Cg is the centroid of ring C16–C20 at (1 – x, –y, 1 – z); (e) x, –1 + y, z; (f) 1 – x, –y, –z.

H atoms were placed in calculated positions and refined using a riding model (C—H = 0.93–0.97 Å), with  $U_{\text{iso}}(\text{H})$  values of 1.2 or 1.5 times  $U_{\text{eq}}(\text{C})$  for aromatic and methyl groups, respectively. Methyl groups were rotated to fit the H-atom positions to the observed electron density. Electron-density difference maps for (II) indicated disorder of a cyclopentadienyl ring attached to Fe1. A two-site disorder model was constructed and refined to give a site-occupation factor of 0.67 (2) for C6–C10 and 0.33 (2) for C47–C51. The final refinement included restraints on the displacement parameters of C6–C10 and C47–C51 (SIMU and DELU; Sheldrick, 1997).

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3044). Services for accessing these data are described at the back of the journal.

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