

C. John McAdam, Brian H. Robinson and Jim Simpson*

Department of Chemistry, University of Otago,
 PO Box 56, Dunedin, New Zealand

Correspondence e-mail:
 jsimpson@alkali.otago.ac.nz

Key indicators

Single-crystal X-ray study
 T = 85 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 R factor = 0.018
 wR factor = 0.078
 Data-to-parameter ratio = 19.7

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

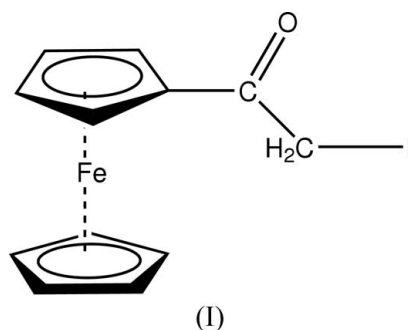
1-Ferrocenyl-2-iodoethanone

The title compound, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_6\text{IO})]$, crystallizes with two unique molecules in the asymmetric unit. Both iodo substituents of the iodoacetyl groups point away from the Fe atoms of the ferrocenyl groups. In the crystal structure, $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds and unusual $\text{I} \cdots \pi$ interactions stabilize the structure.

Received 22 August 2006
 Accepted 23 August 2006

Comment

The title compound, (I), was first reported from the reaction of $\text{CpFe}(\text{CO})_2-\text{CH}_2\text{C}(\text{O})\text{Fc}$ (Fc is ferrocenyl) with iodine by Nesmeyanov *et al.* (1974). A subsequent characterization of iodoacetylferrocene was made by Basetti *et al.* (1985), during a study of the iododemercuration of $(\text{Fc}-\text{C}\equiv\text{C})_2\text{Hg}$. The sample reported here was formed by metathesis of chloroacetylferrocene with sodium iodide in acetone.



Compound (I) crystallizes with two unique molecules, *A* and *B*, in the asymmetric unit. The C16/C111/O1/C112 and C26/C211/O2/C212 planes of the acetyl groups subtend angles of $12.77 (15)^\circ$ and $8.75 (13)^\circ$ to the C11–C15 and C21–C25

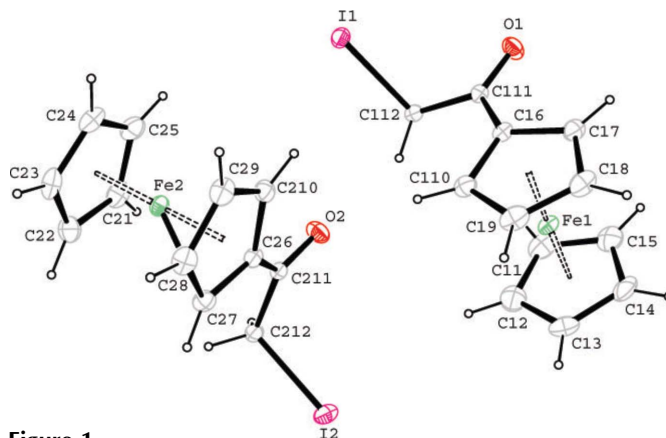


Figure 1
 The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

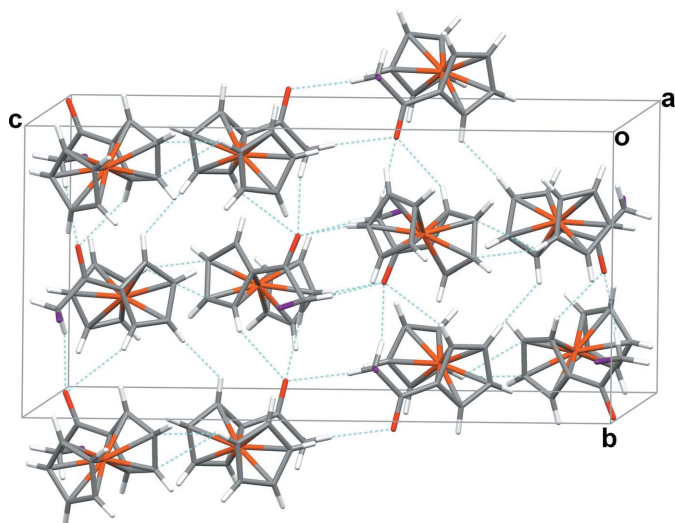


Figure 2
The crystal packing of (I), with C—H···O hydrogen bonds drawn as dashed lines.

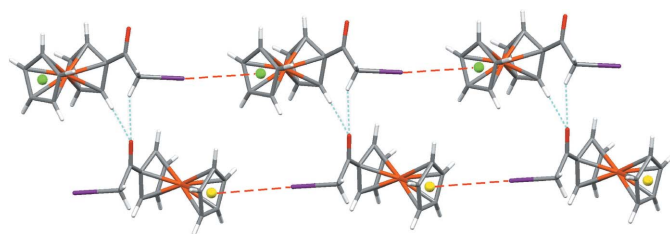


Figure 3
The I1···Cg1A and I2···Cg1B interactions, shown as long dashed lines. Cg1A (green circles) and Cg1B (yellow circles) are the centroids of the C11···C15 and C21···C25 cyclopentadiene rings, respectively. C—H···O hydrogen bonds interconnecting the rows are shown as short dashed lines.

cyclopentadienyl rings, respectively. Both iodo substituents point away from the Fe atoms of the ferrocenyl groups. The cyclopentadienyl rings of each ferrocene are approximately eclipsed, with mean $Cm-Cg1-Cg2-Cn$ torsion angles of $4.9(2)^\circ$ for molecule *A* and $6.0(2)^\circ$ for molecule *B* ($Cg1$ and $Cg2$ are the centroids of the cyclopentadienyl rings, C11–C15 and C16–C110, respectively, for molecule *A*, and C21–C25 and C26–C210, respectively, for molecule *B*; $m = 11-15$ when $n = 16-110$, and $m = 21-25$ when $n = 26-210$). The dihedral angle between the cyclopentadienyl ring planes is $2.31(18)^\circ$ for molecule *A* and $1.31(15)^\circ$ for molecule *B*. The average Fe1–C [$2.047(9)$ Å] and Fe2–C [$2.048(7)$ Å] distances are not unusual and atom Fe1 lies $1.6568(11)$ and $1.6447(10)$ Å, respectively, from the C11–C15 and C16–C110 ring planes in molecule *A*, with the corresponding distances being $1.6556(10)$ and $1.6450(10)$ Å for molecule *B*.

An extensive series of C—H···O hydrogen bonds generates a network structure (Table 1, Fig. 2). In addition, unusual $I \cdots \pi$ interactions link the *A* and *B* molecules into separate rows parallel to the *a* axis, with $I1 \cdots Cg1A^i = 3.774$ Å and $I2 \cdots Cg1B^{ii} = 3.872$ Å (Fig. 3) [Symmetry codes: (i) $1 + x, y, z$; (ii) $-1 + x, y, z$]. These rows are interconnected by C—H···O hydrogen bonds. A search of the Cambridge Structural

Database (Version 5.27; Allen, 2002) for similar $I \cdots \pi$ contacts, with $I \cdots Cg$ distances in the range 3.5–4.0 Å (Cg is the centroid of a cyclopentadienyl ring), revealed three previously reported sets of similar non-bonded interactions, two involving ferrocenyl compounds (Lo *et al.*, 2002; Rodriguez *et al.*, 1997) and the third a cyclopentadienyl tungsten complex (Cheng *et al.*, 1996). Of the three, the packing in the ferrocenyl-*p*-iodophenylethene complex, reported as a weak charge-transfer interaction (Rodriguez *et al.*, 1997), most closely resembles the interactions reported here, with an $I \cdots Cg$ distance of 3.634 Å. Packing was not considered in the other reports.

Experimental

The title compound was prepared as the by-product of a coupling reaction between equimolar amounts of chloroacetylferrocene and piperazine in acetone. The preparation also contained a 7 mol% excess of sodium iodide, the source of metathesized iodine, and potassium carbonate. After refluxing for 4 h, the reaction mixture was filtered and the solvent was removed under vacuum. Column chromatography on silica gel with CH_2Cl_2 eluted 2-iodo-1-ferrocenylethanone as the first band in 8% yield. Characterization was as reported previously (Basetti *et al.*, 1985). Yellow–orange needles of (I) suitable for structural analysis were grown from a solution in CH_2Cl_2 layered with hexane.

Crystal data

[Fe(C ₅ H ₅)(C ₇ H ₆ IO)]	$Z = 8$
$M_r = 353.96$	$D_x = 2.017$ Mg m ⁻³
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.3689(11)$ Å	$\mu = 3.91$ mm ⁻¹
$b = 10.6608(12)$ Å	$T = 85(2)$ K
$c = 21.370(3)$ Å	Rectangular plate, orange
$\beta = 99.252(5)^\circ$	$0.38 \times 0.18 \times 0.08$ mm
$V = 2331.5(5)$ Å ³	

Data collection

Bruker APEXII CCD area-detector diffractometer	34186 measured reflections
φ and ω scans	5352 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	5112 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.470$, $T_{\max} = 0.731$	$R_{\text{int}} = 0.026$
	$\theta_{\max} = 27.6^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 1.3348P]$
$R[F^2 > 2\sigma(F^2)] = 0.018$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\max} = 0.004$
$S = 1.31$	$\Delta\rho_{\max} = 1.37$ e Å ⁻³
5352 reflections	$\Delta\rho_{\min} = -1.38$ e Å ⁻³
271 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C110—H110···O2	0.95	2.67	3.527 (3)	151
C112—H11A···O2	0.99	2.22	3.125 (2)	151
C212—H21B···O1 ⁱ	0.99	2.28	3.232 (3)	161
C27—H27···O1 ⁱ	0.95	2.52	3.349 (3)	146

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

All H atoms bound to carbon were refined using a riding model with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for cyclopentadiene, and C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₂ H atoms. The final difference Fourier map revealed several peaks of approximately 1.0 e Å⁻³ close to the C21–C25 cyclopentadiene ring. However, no obvious chemical significance could be attached to them and they were not investigated further. The deepest hole is located 0.58 Å from atom I1.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) and *TITAN2000* (Hunter & Simpson, 1999); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *enCIFer* (Allen *et al.*, 2004).

The authors thank the New Zealand Foundation for Research Science and Technology for a Postdoctoral Fellowship to CJM, and the Chemistry Department, University of Otago, for financial assistance.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Basetti, M., Floris, B. & Illuminati, G. (1985). *Organometallics*, **4**, 617–623.
- Bruker (2004). *APEX2* (Version 1.017), *SAINTE* (Version 7.12a) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheng, C.-Y., Hsieh, C.-H., Lee, G.-H., Peng, S.-M. & Liu, R. S. (1996). *Organometallics*, **15**, 1565–1571.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hunter, K. A. & Simpson, J. (1999). *TITAN2000*. University of Otago, New Zealand.
- Lo, K. K.-W., Lau, J. S.-Y. & Ng, N. Z. (2002). *Dalton Trans.* pp. 1753–1756.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nesmeyanov, A. N., Perevalova, E. G., Leont'eva, L. I., Eremin, S. A. & Grigor'eva, O. V. (1974). *Izv. Akad. Nauk. SSSR Ser. Khim.* **11**, 2645–2647. (In Russian.)
- Rodriguez, J.-G., Gayo, M. & Fonseca, I. (1997). *J. Organomet. Chem.* **534**, 35–42.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.