O1—C1—C2—O2	109.1 (5)	O1—C1—C11—C15	13.8 (6)
C11—C1—C2—O2	−66.3 (5)	O2—C2—C31—C36	−171.2 (4)
O1—C1—C2—C31	−70.0 (5)	O2—C2—C31—C32	10.4 (6)
O1—C1—C11—C12	−170.5 (4)		

Examination of the structure with *PLATON* (Spek, 1995) showed that there were no solvent-accessible voids in the crystal lattice. The structure was solved by the Patterson heavy-atom method.

Data collection: *CAD-4-PC* (Enraf–Nonius 1992). Cell refinement: *SET4* and *CELDIM* (Enraf–Nonius, 1991). Data reduction: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94* and *PLATON* (Spek, 1995). Software used to prepare material for publication: *NRCVAX94* and *SHELXL93*.

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Racemic Bis(1-ferrocenylpropyl) Ether

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Abstract

The title compound, $[Fe_2(C_5H_5)_2(C_{16}H_{20}O)]$, formed by reduction of propionoylferrocene and subsequent dehydration, crystallizes as a racemic mixture of *RR* and *SS* forms. In the central C—O—C fragment, the angle at the O atom is 115.7 (2)°.

Comment

The reaction between ferrocene and *p*-tolualdehyde in strongly acidic solution yields bis[ferrocenyl(*p*-tolyl)-methyl] ether, $[FcCH(C_6H_4CH_3)]_2O$, [Fc = $(C_5H_5)Fe-(C_5H_4)$] (Matkovic-Calogovic, Rapic & Kovac, 1993). While each of the C atoms bonded to the O atom in this compound is a stereogenic centre, only a single product was isolated, which X-ray structure analysis identified as a racemic mixture of the *RR* and *SS* diastereoisomers (Matkovic-Calogovic *et al.*, 1993). No *RS* or *SR* product was observed. We have now observed that acid-catalysed dehydration of 1-ferrocenylpropan-1-ol, $FcCH(OH)C_2H_5$, yields bis[1-ferrocenylpropyl] ether, $[FcCH(C_2H_5)]_2O$, (I), and have characterized the product as a similar racemic mixture of *RR* and *SS* forms.

(I)
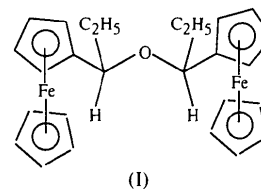
Compound (I) crystallizes in the centrosymmetric triclinic space group P1̄ with one molecule in the asymmetric unit: two enantiomeric forms are therefore present. Structure solution and refinement showed that these were the *RR* and *SS* forms and that each form has approximate twofold rotational symmetry (Fig. 1 and Table 2); no evidence was found for the occurrence of the *meso RS* (or *SR*) form of (I). In this respect, the structure of (I) resembles that of $[FcCH(C_6H_4CH_3)]_2O$, in which the molecules lie on the twofold rotation axes

in the space-group $C2/c$ (Matkovic-Calogovic *et al.*, 1993). Since LiAlH₄ reduction of acylferrocenes FcCOR usually provides the racemic alcohols FcCH(OH)R (Ferguson, Gallagher, Glidewell & Zakaria, 1994; Glidewell, Klar, Lightfoot, Zakaria & Ferguson, 1996), the observation here of only *RR* and *SS* forms indicates effective stereoselectivity in the dehydration process.
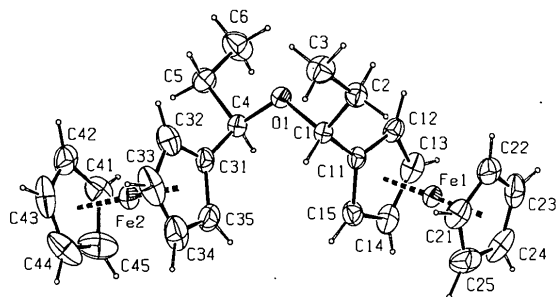

Fig. 1. A view of the *RR* enantiomer of (I) with our numbering scheme. Displacement ellipsoids are drawn at the 30% level.

Within the molecules of (I), the principal features of interest, aside from the configuration at the stereogenic C atoms, are the structure of the central C—O—C bridge and the conformations of the ferrocene fragments. The C—O distances (Table 2) are significantly greater than those of 1.426 (4) Å found in [FcCH(C₆H₄CH₃)]₂O (Matkovic-Calogovic *et al.*, 1993), but the C—O—C angles in the two compounds are virtually identical. Whereas monosubstituted ferrocenes generally exhibit almost perfectly eclipsed cyclopentadienyl rings, in (I) the mean torsion angles C1n—Cg1—Cg2—C2n and C3n—Cg3—Cg4—C4n (*n* = 1–5; the Cg pseudo-atoms are the centroids of the four rings), for the ferrocene groups defined by Fe1 and Fe2, respectively, are −20.8 (2) and −11.6 (4)°; the corresponding value in [FcCH(C₆H₄CH₃)]₂O is reported as 12°.

Experimental

A sample of (I) was prepared by LiAlH₄ reduction of propionoylferrocene, FcCOC₂H₅, followed by chromatography on alumina. TLC and NMR indicated the presence of only a single diastereoisomer. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in dichloromethane/light petroleum. Analysis: found C 66.9, H 6.5%; C₂₆H₃₀Fe₂O requires C 66.4, H 6.4%. NMR (CDCl₃ solution): δ_H 0.80 (*t*, 3H, CH₃), 1.62–1.98 (*m*, 2H, CH₂), 4.15 (*s*, 5H, C₅H₅), 4.05–4.20 p.p.m. (*m*, 5H, C₅H₄ and CH); δ_C 11.0 (*q*, CH₃), 29.3 (*t*, CH₂), 66.2 (*d*), 66.8 (*d*), 67.8 (*d*), 68.4 (*d*), 90.7 (*s*) (C₅H₄), 75.3 p.p.m. (*d*, CH).

Crystal data

[Fe₂(C₅H₅)₂(C₁₆H₂₀O)]
M_r = 470.2

Mo $K\alpha$ radiation
λ = 0.7107 Å

Triclinic
$P\bar{1}$
a = 9.509 (2) Å
b = 10.312 (2) Å
c = 11.541 (2) Å
α = 99.51 (2)°
β = 90.59 (2)°
γ = 100.24 (2)°
V = 1097.4 (4) Å³
Z = 2
D_x = 1.423 Mg m⁻³

Cell parameters from 25 reflections
θ = 18.35–23.00°
μ = 1.336 mm⁻¹
T = 294 (1) K
Block
0.40 × 0.30 × 0.20 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
five ψ scans at 4° steps (North, Phillips & Mathews, 1968)
T_{min} = 0.855, T_{max} = 0.999
4771 measured reflections

4771 independent reflections
3541 observed reflections
$[I > 2\sigma(I)]$
θ_{max} = 26.90°
h = −12 → 11
k = 0 → 13
l = −14 → 14
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0336
$wR(F^2)$ = 0.0869
S = 1.019
4771 reflections
263 parameters
H atoms riding [*SHELXL93* (Sheldrick, 1993) defaults, C—H = 0.93–0.98 Å]
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.2040P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.002

$\Delta\rho_{max}$ = 0.436 e Å⁻³
$\Delta\rho_{min}$ = −0.307 e Å⁻³
Extinction correction:
SHELXL93 (Sheldrick, 1993)
Extinction coefficient:
0.0021 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe1	0.17560 (3)	0.77183 (3)	0.46184 (3)	0.04130 (11)
Fe2	−0.29803 (4)	0.80613 (3)	−0.04003 (3)	0.04772 (11)
O1	−0.2143 (2)	0.5866 (2)	0.24309 (13)	0.0480 (4)
C1	−0.1435 (2)	0.6874 (2)	0.3371 (2)	0.0421 (5)
C2	−0.2136 (2)	0.6526 (3)	0.4486 (2)	0.0538 (6)
C3	−0.3735 (3)	0.6514 (3)	0.4455 (3)	0.0707 (8)
C4	−0.1899 (3)	0.6144 (2)	0.1264 (2)	0.0476 (5)
C5	−0.2522 (3)	0.4854 (2)	0.0444 (2)	0.0621 (7)
C6	−0.1837 (4)	0.3679 (3)	0.0622 (3)	0.0839 (10)
C11	0.0154 (2)	0.6892 (2)	0.3363 (2)	0.0419 (5)
C12	0.0866 (3)	0.5899 (2)	0.3668 (2)	0.0506 (6)
C13	0.2332 (3)	0.6241 (3)	0.3437 (2)	0.0633 (7)
C14	0.2544 (3)	0.7435 (3)	0.2993 (2)	0.0687 (8)
C15	0.1192 (3)	0.7853 (3)	0.2942 (2)	0.0580 (7)
C21	0.1073 (3)	0.8988 (3)	0.5947 (2)	0.0688 (8)
C22	0.1265 (3)	0.7831 (3)	0.6347 (2)	0.0701 (8)
C23	0.2695 (4)	0.7692 (4)	0.6202 (3)	0.0835 (10)
C24	0.3378 (3)	0.8769 (4)	0.5735 (3)	0.0853 (11)
C25	0.2386 (4)	0.9574 (3)	0.5570 (3)	0.0834 (10)
C31	−0.2536 (3)	0.7337 (2)	0.1088 (2)	0.0540 (6)
C32	−0.4006 (3)	0.7391 (3)	0.0986 (2)	0.0704 (8)
C33	−0.4138 (5)	0.8735 (4)	0.0954 (3)	0.0934 (12)
C34	−0.2792 (6)	0.9496 (4)	0.1044 (3)	0.1039 (15)

C35	−0.1790 (4)	0.8652 (3)	0.1118 (3)	0.0891 (11)
C41	−0.2202 (4)	0.7031 (3)	−0.1835 (2)	0.0706 (8)
C42	−0.3697 (4)	0.6788 (4)	−0.1917 (2)	0.0797 (9)
C43	−0.4135 (5)	0.8047 (5)	−0.1885 (3)	0.0978 (13)
C44	−0.2943 (5)	0.8992 (4)	−0.1807 (3)	0.1002 (13)
C45	−0.1735 (4)	0.8391 (4)	−0.1771 (3)	0.1015 (13)

Table 2. *Selected geometric parameters (Å, °)*

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the four cyclopentadienyl rings, calculated from the positions of the constituent atoms.

Fe1—*Cg*1	1.644 (2)	Fe2—*Cg*4	1.645 (2)
Fe1—*Cg*2	1.654 (2)	O1—C1	1.440 (2)
Fe2—*Cg*3	1.641 (2)	O1—C4	1.435 (3)
*Cg*1—Fe1—*Cg*2	177.9 (1)	C1—O1—C4	115.7 (2)
*Cg*3—Fe2—*Cg*4	177.7 (1)		
C4—O1—C1—C11	−69.9 (2)	O1—C4—C5—C6	−60.0 (3)
C4—O1—C1—C2	166.4 (2)	C31—C4—C5—C6	178.6 (2)
O1—C1—C2—C3	−59.3 (3)	O1—C1—C11—C12	−70.2 (3)
C11—C1—C2—C3	−179.8 (2)	C2—C1—C11—C12	47.9 (3)
C1—O1—C4—C31	−65.6 (2)	O1—C4—C31—C32	−70.9 (3)
C1—O1—C4—C5	170.1 (2)	C5—C4—C31—C32	47.9 (3)

Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* (Enraf–Nonius, 1991). Data reduction: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX94*. Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*, *PLATON* (Spek, 1995*a*) and *PLUTON* (Spek, 1995*b*). Software used to prepare material for publication: *NRCVAX94* and *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Mn$_4^{III}$(μ_3-O)$_2$(μ-O$_2$CMe)$_7$(2,2'-bipyridine)$_2$]ClO$_4$

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Abstract

The anhydrous form of a known tetramanganese cluster, which was previously isolated in its trihydrate form, has been prepared from a different starting material. The new complex, bis(μ_3-oxo)-1:2:4κ^3*O*;2:3:4κ^3*O*-heptakis(μ-acetato)-1:2κ^4*O*:*O*';1:4κ^2*O*:*O*';2:3κ^2*O*:*O*';2:4κ^2-*O*:*O*';3:4κ^4*O*:*O*'-bis(2,2'-bipyridine)-1κ^2*N,N*';3κ^2*N,N*'-tetramanganese perchlorate, [Mn$_4$(O)$_2$(C$_2$H$_3$O$_2$)$_7$-(C$_{10}$H$_8$N$_2$)$_2$]ClO$_4$, crystallizes in the monoclinic space group *C2/c*, in a higher symmetry compared to the previous form. A crystallographic twofold axis passes through the centre of the molecule. The fundamental structure of the complex clearly resembles that of the form already reported.

Comment

Vincent *et al.* (1989) previously reported a variety of tetramanganese clusters as synthetic models for the O$_2$-evolving centre in Photosystem II. They prepared a tetramanganese(III) complex, [Mn$_4$(μ_3-O)$_2$(μ-O$_2$CMe)$_7$(bpy)$_2$]ClO$_4$.3H$_2$O (bpy = 2,2'-bipyridine), from the reaction of [Mn$_3$(μ_3-O)(μ-O$_2$CMe)$_6$-(pyridine)$_3$]ClO$_4$ with bpy. We report here the anhydrous form of this complex, (I). In the preparation of the title complex, [Mn$_3$(μ_3-O)(μ-O$_2$CMe)$_6$(OH$_2$)$_3$]-MeCO$_2$ was employed in place of the starting trimer having pyridines in the terminal sites. Although Vincent *et al.* (1989) paid attention to the use of pyridine in the syntheses of such complexes, this result suggests that the presence of pyridine is not essential for the formation of the complex. Their trihydrate form crystallizes in the triclinic space group *P*1̄ and the tetramanganese

(I)