Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and contact distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71482 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1057]

References

Alyea, E. C., Ferguson, G., Jennings, M. C., Li, B., Xu, Z., You, X.-Z. & Liu, S. (1990). *Polyhedron*, **9**, 739-741.
Alyea, E. C., Ferguson, G., Jennings, M. C. & Xu, Z. (1990). *Acta Cryst.* C**46**, 2347-2349.
Alyea, E. C., Liu, S., Li, B., Xu, Z. & You, X.-Z. (1989). *Acta Cryst.* C**45**, 1566-1568.
Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384-387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Acta Cryst. (1994). C**50**, 18–23

Hydrogen-Bonding Patterns in Ferrocene Derivatives: Structures of 1,1′-Diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol and 1,1′-(1,1′-Ferrocenediyl)diethanol

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Abstract

Racemic 1,1′-diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(Ph)MeOH}$_2$] (I), crystallizes as hydrogen-bonded dimeric aggregates with the Fe atoms on twofold crystallographic axes and the four O atoms defining a folded trapezium with O···O distances of 2.784 (2) (×2), 2.877 (3) and 2.795 (4) Å. The four hydroxyl H atoms are disordered equally over two orientations such that there are two half-occupancy H-atom sites between each hydrogen-bonded O-atom pair. Racemic 1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(H)MeOH}$_2$] (II), crystallizes as hydrogen-bonded centrosymmetric dimers, with O···O distances of 2.778 (2) and 2.764 (2) Å and ordered hydroxyl H atoms. In (I), the dimers are formed from either two *RR* or two *SS* molecules, while in (II) the dimers each contain one *RR* and one *SS* molecule.

Comment

We are currently studying the molecular structures and hydrogen-bonding patterns in the crystal lattices of ferrocene–alcohol derivatives. The diol, ferrocene-1,1′-diylbis(diphenylmethanol), [Fe{(C_5H_4)C(Ph)$_2$OH}$_2$] (III) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*), crystallizes with the asymmetric unit comprising two independent half molecules lying on crystallographic twofold axes; these molecules form dimeric aggregates held together by a hydrogen-bonded motif with graph set $R_4^4(8)$ (Etter, MacDonald & Bernstein, 1990), in which the hydroxyl H atoms are all disordered equally over two sites.

The monoalcohols 1,1′-bis(ferrocenyl)-2,2′-dimethylpropan-1-ol, [(C_5H_5)Fe(C_5H_4)]$_2$C(CMe$_3$)OH (Sharma, Cervantes-Lee & Pannell, 1992), and ferrocenyl(diphenyl)methanol, [(C_5H_5)Fe(C_5H_4)]CPh$_2$OH (IV) (Ferguson, Gallagher, Glidewell & Zakaria, 1993), crystallize as hydrogen-bonded dimeric aggregates with a hydrogen-bonded motif characterized by the graph set $R_2^2(4)$. However, in racemic 1-ferrocenyl-1-phenylethanol, [(C_5H_5)-Fe(C_5H_4)]CPhMeOH (V), where the steric demands about the central C atom are considerably less, there is no O—H···O hydrogen bonding in the crystal structure (Ferguson, Gallagher, Glidewell & Zakaria, 1993).

The extent and nature of the hydrogen bonding in ferrocenyl monoalcohols of the type [(C_5H_5)Fe(C_5H_4)]-C$R'R''$OH is clearly not a function solely of the steric demands about the central C atom, as appears to be the case in, for example, the series $(Ph)_x(PhCH_2)_{3-x}COH$ (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992; Ferguson, Gallagher, Glidewell & Zakaria, 1994). Hence, in order to assess further the effects on the hydrogen-bonding patterns in the crystal structures of ferrocenediols by the changes in substituents at the central C atom, we have determined the structures of 1,1′-diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(Ph)-MeOH}$_2$] (I), and 1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(H)MeOH}$_2$] (II).

[Fe{(C_5H_4)C(Ph)MeOH}$_2$] (I) crystallizes in the centrosymmetric space group *C*2/*c* with two independent half molecules in the asymmetric unit; both Fe atoms lie on a crystallographic twofold axis. The molecules are hydrogen bonded to form a dimeric structural motif with graph set $R_4^4(8)$ (Fig. 1). The O atoms form a flattened trapezium with hydrogen-bonded O···O distances 2.784 (2) (×2), 2.877 (3) and 2.795 (4) Å. Difference maps showed that within the dimeric aggregate, the hydroxyl H atoms are each disordered equally over two sites, while directed towards the two neighbouring hydroxyl O atoms, as shown

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in Figs. 1 and 2. The four O—H distances (H-atom coordinates from difference maps) are in the range 0.64-0.69 Å, and the four C—O—H angles lie between 110 and 123° (the two H—O—H angles are 116 and 127°).

Within any dimeric aggregate, all four stereogenic centers are of the same chirality, *R* or *S*; but, related to any such dimer by the action of a center of inversion is another dimer where all four stereogenic centers have the opposite chirality, *S* or *R*. Hence, each dimer is formed either from two *RR* molecules or from two *SS* molecules; no *RS* (or *SR*) molecules are present, so that (I) represents the racemic (*threo*) rather than the *meso* (*erythro*) form. ^{1}H and ^{13}C NMR studies of the crude mixture from the reaction of 1,1′-diacetylferrocene with phenyllithium showed the presence of only a single diastereoisomer; thus the *R* or *S* configuration of the first-formed stereogenic center in this reaction determines completely the stereochemical course of the formation of the second stereogenic center. Within each dimer (whether formed from *RR* or from *SS* molecules), the positional disorder of the hydroxyl H atoms demands that the hydrogen bonds describe either a clockwise or a counter-clockwise pattern, as found previously for [Fe{(C_5H_4)CPh_2OH}$_2$] (III) (Ferguson, Gallagher, Glidewell & Zakaria, 1993). There are thus two forms, present in equal numbers, for both the *RR* dimers and the *SS* dimers, generating a total of four different types of dimeric aggregate within the crystal structure of racemic (I).

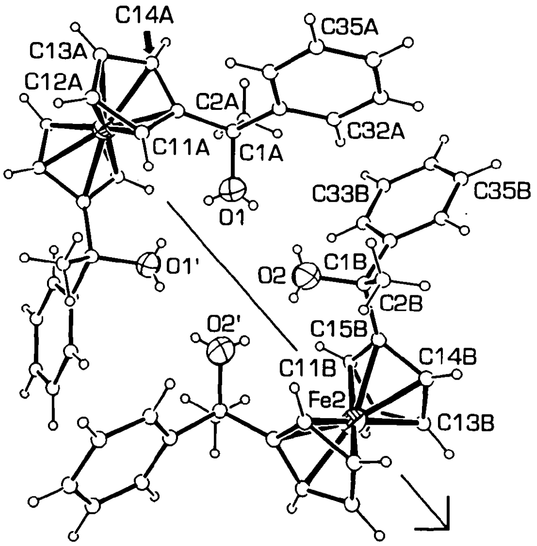

Fig. 1. A view of 1,1′-diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol (I) as the hydrogen-bonded dimeric aggregate. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity, H atoms are drawn as small spheres of arbitrary size.

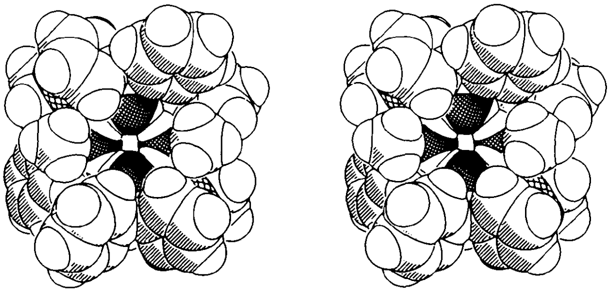

Fig. 2. A stereoview of the dimeric aggregate of molecule (I) with atoms depicted as their van der Waals spheres.

The Fe—C bond lengths in (I) are in the range 2.029 (2)-2.052 (2) Å [mean 2.041 (2) Å] and 2.023 (2)-2.053 (2) Å [mean 2.041 (2) Å], for molecules *A* and *B*, respectively. The C_{sp^3}—O bond lengths are 1.437 (2) and 1.424 (3) Å. The dihedral angles between the symmetry-related C_5 planes in each molecule are both 3.9 (1)°. These C_5 rings are within 2.2 (1) (molecule *A*) and 3.0 (1)° (molecule *B*) of being eclipsed. The conformation adopted by both molecules of (I) is such that the exocyclic C_{sp^3} atoms are rotated about a line joining the ring centroids through 69.4 (1) (molecule *A*) and 66.7 (1)° (molecule *B*) from an eclipsed conformation [the values reported for (III) are −66.5 (2) and 62.1 (2)°]. These C_{sp^3} carbon atoms, C1*A* and C1*B*, are displaced 0.082 (5) and 0.080 (5) Å from the plane of their respective C_5 rings away from the Fe atom.

The phenyl-ring orientations in molecules *A* and *B* are almost normal to the ferrocene system with C11*A*—C15*A*—C1*A*—C31*A* −85.0 (2) and C11*B*—C15*B*—C1*B*—C31*B* −84.0 (2)°. In molecule *A*, the phenyl ring is oriented so that it is almost parallel to the exocyclic C15*A*—C1*A* bond [C15*A*—C1*A*—C31*A*—C32*A* −174.8 (2)°], whereas in molecule *B*, the phenyl ring is normal to the C15*B*—C1*B* bond [C15*B*—C1*B*—C31*B*—C32*B* 85.4 (2)°]. Presumably the different phenyl-ring orientations in molecules *A* and *B* allow better intermolecular packing. The C15*A*—C1*A*—C31*A* and C15*B*—C1*B*—C31*B* angles are different [111.1 (2) and 108.6 (2)°, respectively] as a result of repulsion between the *ortho* H(36*A*) and C15*A* (H···C 2.46 Å). The other three corresponding O—C_{sp^3}—C_{sp^3} angles in *A* and B are identical with differences < 0.3 (2)°. The ferrocene moieties of (I) are almost normal to one another; the angle between the C_5 symmetry axes of the ferrocene moieties is −84.5° (Fig. 1) [51.9° in (III)]. In the crystal lattice, the contacts between dimers correspond to normal van der Waals interactions.

The asymmetric unit of 1,1′-(1,1′-ferrocenediyl)diethanol (II) consists of a single molecule, in which the two stereogenic centers have the same chirality; these molecules form centrosymmetric hydrogen-bonded dimers with fully ordered hydroxyl H atoms and graph set $R^4_4(8)$, (Fig. 3). There is thus only one type of dimer in the crystal structure, as opposed to four in the crystal structure of (I). Each dimer is made up from one *RR* molecule and one *SS* molecule [in the crystal structure of (I), the *RR* and *SS* molecules occur in different dimers]. Since there are no *RS* (= *SR*) molecules in the crystal of (II), this diastereoisomer is the racemic rather than the *meso* form.

Crystals produced in precisely the same manner as those of (II) and having an identical melting point were assigned the *meso* configuration by Yamakawa & Hisatome (1973); the basis for this assignment is uncertain, but it is clearly incorrect. Within the dimeric aggregate of (II), the O$\cdots$O distances are 2.778 (2) and 2.764 (2) Å. The O—H distances are 0.82 and 0.78 Å, while the C—O—H angles are 108 and 109°.

The Fe—C bond lengths in (II) are in the range 2.041 (1)-2.050 (1) Å [mean 2.047 (1) Å] for ring C11—C15 and 2.045 (1)-2.047 (1) Å [mean 2.046 (1) Å] for ring C21—C25. The C_{sp^3}—O bond lengths of 1.429 (2) and 1.431 (2) Å and the range and mean of C_{ar}—C_{ar} bond lengths for both rings [1.414 (2)-1.428 (2), 1.423 (2) Å and 1.412 (2)-1.428 (2), 1.422 (2) Å, repectively] are similar to those in (I). The interplanar angle between the cyclopentadienyl planes is 1.1 (1)° and these rings are within 6.8 (1)° of being eclipsed. The conformation adopted is such that the exocyclic C_{sp^3} atoms are rotated about a line joining the ring centroids through 65.8 (1)° from an eclipsed conformation. The C_{sp^3} atoms C1*A* and C1*B* are displaced 0.091 (3) and 0.065 (3) Å from the plane of their respective C_5 rings, away from the Fe atom. As the dimeric aggregate is centrosymmetric, the two ferrocene systems are precisely parallel.

There is no solvent of crystallization present in either of the lattices and an examination of the crystal structures using *PLATON* (Spek, 1991) revealed no potential volume for any solvent molecules.

Shubina and co-workers in a series of papers (Shubina, Epstein, Yanovsky, Timofeeva, Struchkov, Kreindlin, Fadeeva & Rybinskaya, 1988; Shubina, Epstein, Timofeeva, Struchkov, Kreindlin, Fadeeva & Rybinskaya, 1991; Shubina, Epstein, Kreindlin, Fadeeva & Rybinskaya, 1991) have studied the hydrogen bonding in a series of metallocenylcarbinols, primarily by infrared spectroscopy. In addition to bands assignable to OH$\cdots$O hydrogen bonds, other spectral features in the OH stretching region have been observed; both OH$\cdots M$ and OH$\cdots\pi(C_5R_5)$ interactions have been considered to be responsible for these. These bands, originally assigned (Shubina, Epstein, Yanovsky, Timofeeva, Struchkov, Kreindlin, Fadeeva & Rybinskaya, 1988) as OH$\cdots\pi(C_5R_5)$, were subsequently reassigned as OH$\cdots M$ interactions (Shubina, Epstein, Kreindlin, Fadeeva & Rybinskaya, 1991). The basis of these assignments appears to be far from secure. In (I) and (II), the intra- and intermolecular O—H$\cdots$O hydrogen bonding is clearly the driving force towards formation of the dimeric aggregate. However, in racemic 1-ferrocenyl-1-phenylethanol, $[(C_5H_5)Fe(C_5H_4)]CPhMeOH$ (V), where there is no O—H$\cdots$O hydrogen bonding, and in ferrocenyl(diphenyl)methanol, $[(C_5H_5)Fe(C_5H_4)]CPh_2OH$ (IV), where the O—H$\cdots$O hydrogen bonding is characterized by the graph set $R_2^2(4)$ (Ferguson, Gallagher, Glidewell & Zakaria, 1993), it is possible that there are weak O—H$\cdots C_{cp}$ interactions (Table 2). OH$\cdots M$ interactions have also been inferred from a number of independent X-ray crystallographic studies (Lecomte, Dusausoy, Protas, Moïse & Tirouflet, 1973; Struchkov, Batsanov, Toma & Salisova, 1987; Shubina, Epstein, Slovokhotov, Mironov, Stuchkov, Kaganovich, Kreindlin & Rybinskaya, 1991), but in every case the structural data are at least as consistent with the occurrence of O—H$\cdots$O or O—H$\cdots\pi(C_5R_5)$ interactions as with O—H$\cdots M$ hydrogen bonding. The occurrence of OH$\cdots M$ interactions in all of these compounds must be regarded as 'not proven'.

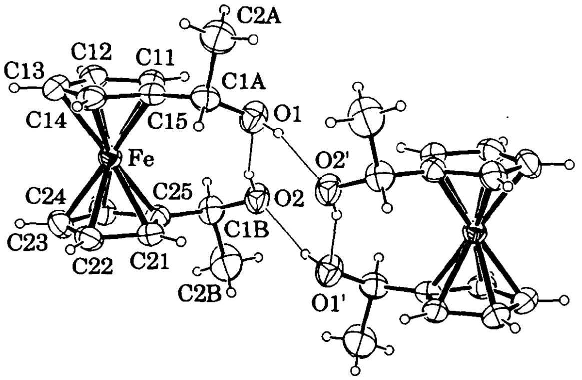

Fig. 3. A view of 1,1′-(1,1′-ferrocenediyl)diethanol (II) as the hydrogen-bonded dimeric aggregate. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity, H atoms are drawn as small spheres of arbitrary size.

In the dimeric units in each of the diols (I), (II) and 1,1′-ferrocenediylbis(diphenylmethanol) (III) (Ferguson, Gallagher, Glidewell & Zakaria, 1993), as well as in the dimers of ferrocenyl(diphenyl)methanol (Ferguson, Gallagher, Glidewell & Zakaria, 1993) and 1,1′-bis(ferrocenyl)-2,2′-dimethylpropan-2-ol (Sharma, Cervantes-Lee & Pannell, 1992), the hydrogen-bonded array of hydroxyl groups is always essentially planar, as is generally true of such arrays; however, a folded hydrogen-bonded dimer based on an $R_2^2(10)$ motif, with a fold angle of 101°, has been described recently (Perkins, Setchell & Williams, 1993) and appropriate molecular design should be capable of generating such structures within the electroactive ferrocene series.

Experimental

Compound (I)

Crystal data

$[Fe(C_{13}H_{13}O)_2]$
$M_r = 426.33$
Monoclinic
$C2/c$
$a = 14.7334$ (8) Å
$b = 21.7592$ (15) Å
$c = 14.7830$ (9) Å
$\beta = 117.273$ (4)°

$D_x = 1.345$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.0$- 18.0°
$\mu = 0.73$ mm^{-1}
$T = 293$ K
Block

$V = 4212.4$ (4) Å^3
$Z = 8$

0.40 × 0.30 × 0.20 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.772$, $T_{\max} = 0.847$
4759 measured reflections
4591 independent reflections

3192 observed reflections
$[I_{\rm net} > 3.0\sigma(I_{\rm net})]$
$R_{\rm int} = 0.011$
$\theta_{\max} = 27.0°$
$h = -18 \rightarrow 16$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.030$
$wR = 0.043$
$S = 1.45$
3192 reflections
292 parameters
Only H-atom U's refined; H(O) from Δ map, H(C) riding at 0.95 Å
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 7085 (1051)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for compound* (I)

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

	x	y	z	$U_{\rm eq}$
Fe1	$\frac{1}{2}$	0.476463 (19)	$\frac{1}{4}$	0.0496 (3)
O1	0.51257 (12)	0.32645 (7)	0.15906 (12)	0.0486 (10)
C1*A*	0.50166 (14)	0.37593 (9)	0.09040 (14)	0.0379 (11)
C2*A*	0.38904 (17)	0.38411 (13)	0.01495 (18)	0.0583 (17)
C11*A*	0.62655 (18)	0.43440 (10)	0.25428 (18)	0.0492 (14)
C12*A*	0.64699 (25)	0.49712 (14)	0.28418 (24)	0.0764 (23)
C13*A*	0.5802 (3)	0.53373 (12)	0.2040 (3)	0.086 (3)
C14*A*	0.51649 (23)	0.49494 (11)	0.12377 (21)	0.0627 (19)
C15*A*	0.54484 (16)	0.43275 (9)	0.15450 (16)	0.0419 (13)
C31*A*	0.56258 (15)	0.35872 (8)	0.03352 (15)	0.0375 (11)
C32*A*	0.52971 (20)	0.31069 (12)	−0.03578 (21)	0.0630 (18)
C33*A*	0.58224 (24)	0.29440 (14)	−0.08968 (24)	0.0780 (22)
C34*A*	0.66764 (21)	0.32563 (13)	−0.07614 (21)	0.0699 (19)
C35*A*	0.70172 (18)	0.37328 (13)	−0.00768 (20)	0.0614 (17)
C36*A*	0.64977 (16)	0.38941 (10)	0.04677 (16)	0.0470 (13)
Fe2	$\frac{1}{2}$	0.049504 (18)	$\frac{1}{4}$	0.0438 (3)
O2	0.47631 (14)	0.20043 (8)	0.14701 (14)	0.0610 (13)
C1*B*	0.48485 (16)	0.15250 (10)	0.08573 (16)	0.0462 (13)
C2*B*	0.59569 (20)	0.14704 (17)	0.10590 (23)	0.0804 (22)
C11*B*	0.36959 (16)	0.09146 (10)	0.14426 (17)	0.0466 (12)
C12*B*	0.35022 (21)	0.02885 (12)	0.15715 (21)	0.0658 (16)
C13*B*	0.41480 (23)	−0.00729 (11)	0.13331 (21)	0.0732 (20)
C14*B*	0.47489 (21)	0.03193 (12)	0.10518 (19)	0.0621 (16)
C15*B*	0.44733 (15)	0.09396 (9)	0.11310 (16)	0.0435 (12)
C31*B*	0.41335 (16)	0.16810 (10)	−0.02574 (16)	0.0450 (12)
C32*B*	0.32472 (17)	0.20113 (11)	−0.05109 (18)	0.0545 (15)
C33*B*	0.26095 (20)	0.21801 (13)	−0.15006 (21)	0.0665 (17)
C34*B*	0.28343 (23)	0.20139 (13)	−0.22701 (20)	0.0717 (18)
C35*B*	0.3690 (3)	0.16772 (16)	−0.20437 (21)	0.0828 (24)
C36*B*	0.43426 (22)	0.15096 (14)	−0.10452 (20)	0.0713 (19)

Table 2. *Geometric parameters* (Å) *for compound* (I)

Fe1—C11A	2.0519 (23)	Fe2—C11*B*	2.0533 (21)
Fe1—C12*A*	2.036 (3)	Fe2—C12*B*	2.044 (3)
Fe1—C13*A*	2.0363 (25)	Fe2—C13*B*	2.0234 (24)
Fe1—C14*A*	2.0294 (22)	Fe2—C14*B*	2.0349 (25)
Fe1—C15*A*	2.0467 (18)	Fe2—C15*B*	2.0480 (21)
O1—C1*A*	1.4374 (24)	O2—C1*B*	1.424 (3)
C1*A*—C2*A*	1.527 (3)	C1*B*—C2*B*	1.524 (3)
C1*A*—C15*A*	1.510 (3)	C1*B*—C15*B*	1.516 (3)
C1*A*—C31*A*	1.531 (3)	C1*B*—C31*B*	1.533 (3)
C11*A*—C12*A*	1.423 (3)	C11*B*—C12*B*	1.423 (3)
C11*A*—C15*A*	1.414 (3)	C11*B*—C15*B*	1.418 (3)
C12*A*—C13*A*	1.392 (6)	C12*B*—C13*B*	1.398 (5)
C13*A*—C14*A*	1.407 (4)	C13*B*—C14*B*	1.422 (4)
C14*A*—C15*A*	1.428 (3)	C14*B*—C15*B*	1.430 (3)
C31*A*—C32*A*	1.386 (3)	C31*B*—C32*B*	1.383 (3)
C31*A*—C36*A*	1.380 (3)	C31*B*—C36*B*	1.385 (3)
C32*A*—C33*A*	1.387 (3)	C32*B*—C33*B*	1.378 (4)
C33*A*—C34*A*	1.362 (4)	C33*B*—C34*B*	1.371 (4)
C34*A*—C35*A*	1.373 (4)	C34*B*—C35*B*	1.360 (5)
C35*A*—C36*A*	1.386 (3)	C35*B*—C36*B*	1.391 (4)
O1—H1	0.651	O2—H3	0.693
O1—H2	0.644	O2—H4	0.647

Compound (II)

Crystal data

$[\mathrm{Fe(C_7H_9O)_2}]$
$M_r = 274.14$
Monoclinic
$P2_1/c$
$a = 6.1096$ (3) Å
$b = 16.5931$ (8) Å
$c = 12.7382$ (5) Å
$\beta = 95.373$ (4)°
$V = 1285.69$ (10) Å^3
$Z = 4$
$D_x = 1.416$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 16.0\text{-}20.0°$
$\mu = 1.16$ mm^{-1}
$T = 293$ K
Block
0.65 × 0.40 × 0.35 mm
Light orange

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.715$, $T_{\max} = 0.772$
8737 measured reflections
4443 independent reflections

3588 observed reflections
$[I_{\rm net} > 3.0\sigma(I_{\rm net})]$
$R_{\rm int} = 0.009$
$\theta_{\max} = 32.0°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.026$
$wR = 0.042$
$S = 1.51$
3588 reflections
173 parameters
Only H-atom U's refined; H(O) from Δ map, H(C) riding at 0.95 Å
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 6041 (697)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for compound* (II)

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

	x	y	z	U_{eq}
Fe	0.76739 (3)	0.483929 (10)	0.193869 (13)	0.02988 (8)
O1	0.63863 (21)	0.40165 (7)	0.44470 (9)	0.0500 (5)
O2	0.74213 (20)	0.56439 (6)	0.46261 (8)	0.0469 (5)
C1*A*	0.58376 (24)	0.35415 (8)	0.35245 (11)	0.0399 (6)
C2*A*	0.60820 (41)	0.26464 (10)	0.37880 (17)	0.0662 (11)
C11	0.95348 (20)	0.40508 (8)	0.28841 (10)	0.0357 (5)
C12	1.03927 (22)	0.41308 (9)	0.18850 (11)	0.0424 (6)
C13	0.87426 (26)	0.38936 (9)	0.10930 (11)	0.0441 (6)
C14	0.68532 (24)	0.36665 (8)	0.15907 (11)	0.0396 (6)
C15	0.73296 (20)	0.37656 (7)	0.27023 (10)	0.0341 (5)
C1*B*	0.85300 (24)	0.60790 (9)	0.38628 (11)	0.0420 (6)
C2*B*	0.82828 (45)	0.69664 (11)	0.41107 (16)	0.0725 (13)
C21	0.54098 (20)	0.56238 (8)	0.24433 (10)	0.0349 (5)
C22	0.51780 (24)	0.55688 (8)	0.13198 (10)	0.0412 (6)
C23	0.71860 (28)	0.58065 (9)	0.09471 (11)	0.0457 (7)
C24	0.86740 (25)	0.60099 (9)	0.18307 (11)	0.0416 (6)
C25	0.75817 (21)	0.58957 (7)	0.27612 (10)	0.0343 (5)
HO1	0.529	0.404	0.478	0.089 (8)
HO2	0.732	0.519	0.445	0.044 (5)

Table 4. *Geometric parameters* (Å) *for compound* (II)

Fe—C11	2.0490 (12)	C11—C12	1.4272 (19)
Fe—C12	2.0413 (13)	C11—C15	1.4263 (18)
Fe—C13	2.0448 (14)	C12—C13	1.4137 (21)
Fe—C14	2.0477 (13)	C13—C14	1.4190 (23)
Fe—C15	2.0500 (13)	C14—C15	1.4280 (19)
Fe—C21	2.0463 (12)	C1*B*—C2*B*	1.5166 (24)
Fe—C22	2.0462 (13)	C1*B*—C25	1.4983 (19)
Fe—C23	2.0469 (14)	C21—C22	1.4277 (18)
Fe—C24	2.0447 (14)	C21—C25	1.4240 (18)
Fe—C25	2.0456 (13)	C22—C23	1.4125 (23)
O1—C1*A*	1.4286 (18)	C23—C24	1.4198 (21)
O2—C1*B*	1.4312 (18)	C24—C25	1.4263 (19)
C1*A*—C2*A*	1.5270 (22)	O1—HO1	0.823
C1*A*—C15	1.4983 (20)	O2—HO2	0.785

Table 5. *Shortest interatomic distances in ferrocenyl alcohol derivatives* (Å)

C_{cp} is the closest cyclopentadienyl C atom to the hydroxyl H atom; Fc is ferrocenyl.

Molecule	O···O	O···C_{cp}	O···Fe
(I) Fc[C(Me)(Ph)OH$_2$][a]	2.877 (3)	3.710 (3)	3.567 (2)
A	2.784 (2)	3.725 (3)	3.569 (2)
B	2.795 (4)		
(II) Fc[C(Me)(H)OH$_2$][a]	2.778 (2)	3.701 (2)	3.628 (1)
	2.764 (2)	3.757 (2)	3.691 (1)
(III) Fc(CPh$_2$OH)$_2$	2.714 (3)	3.403 (3)	3.440 (1)
A	2.762 (2)	3.871 (3)	3.591 (1)
B	2.865 (4)		
(IV) Fc(CPh$_2$OH)	2.816 (2)	3.533 (2)	3.559 (1)
(V) Fc[CMe(Ph)OH]	3.768 (3)	3.480 (4)	3.463 (2)
Co$_4$(CO)$_9$(η^6-PhCHOHFc)[b]	2.93 (1)	—	3.466 (5)
FcC(OH)(PhC$_4$O$_2$)[c]	3.661 (4)	3.605 (5)	3.527 (3)
(CH$_2$)$_3$Fc[PhC(OH)Et][d]	2.89 (2)	3.15 (2)	3.44 (1)

References: (*a*) present work; (*b*) Shubina, Epstein, Slovokhotov, Mironov, Struchkov, Kaganovich, Kreindlin & Rybinskaya (1991); (*c*) Struchkov, Batsanov, Toma & Salisova (1987); (*d*) Lecomte, Dusausoy, Protas, Moïse & Tirouflet (1973).

1,1′-Diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol (I) was obtained from the reaction of 1,1′-diacetylferrocene with phenyllithium; crystals were grown by slow evaporation of a solution in hexane. 1,1′-(1,1′-Ferrocenediyl)diethanol (II) was synthesized as a diastereoisomeric mixture (m.p. 342-343 K) by lithium aluminium hydride reduction of 1,1′-diacetylferrocene; fractional crystallization from hexane (Yamakawa & Hisatome, 1973) provided (II) (m.p. 372-373 K), characterized as a single diastereoisomer by ^{1}H and ^{13}C NMR spectroscopy. Single crystals were grown by slow evaporation of a solution in hexane.

The systematic absences for (I) (hkl absent if $h + k = 2n + 1$, $h0l$ absent if $l = 2n + 1$) allow the space group to be either $C2/c$ or Cc; the former was assumed and confirmed by the analysis. The space group for (II) was determined unambiguously from the systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$) as $P2_1/c$. In both structures, the H atoms attached to the C atoms were clearly visible in difference maps and were positioned on geometric grounds (C—H 0.95 Å); they were included as riding atoms in the structure-factor calculations. The hydroxyl H atoms [disordered equally in (I) over two sites] were included in the structure-factor calculations at the positions obtained from difference maps. The thermal parameters of all H atoms were refined. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*; *ORTEP*II (Johnson, 1976); *PLUTON* (Spek, 1991). Software used to prepare material for publication: *NRCVAX TABLES*.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71461 (56 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1056]

References

Enraf-Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256-262.

Ferguson, G., Gallagher, J. F., Glidewell, C., Low, J. N. & Scrimgeour, S. N. (1992). *Acta Cryst.* **C48**, 1272-1275.

Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1993). *Acta Cryst.* **C49**, 967-971.

Ferguson, G.,Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1994). *Acta Cryst.* **C50**, 70-73.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384-387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291-294. Copenhagen: Munksgaard.

Lecomte, C., Dusausoy, Y., Protas, J., Moïse, C. & Tirouflet, J. (1973). *Acta Cryst.* **B29**, 488-493.

Perkins, M. J., Setchell, P. K. & Williams, D. J. (1993). *J. Chem. Soc. Chem. Commun.* pp. 128-129.
Sharma, H. K., Cervantes-Lee, F. & Pannell, K. H. (1992). *J. Organomet. Chem.* **438**, 183-194.
Shubina, E. S., Epstein, L. M., Kreindlin, A. Z., Fadeeva, S. S. & Rybinskaya, M. I. (1991). *J. Organomet. Chem.* **401**, 145-153.
Shubina, E. S., Epstein, L. M., Slovokhotov, Yu. L., Mironov, A. V., Struchkov, Yu. T., Kaganovich, V. S., Kreindlin, A. Z. & Rybinskaya, M. I. (1991). *J. Organomet. Chem.* **401**, 155-165.
Shubina, E. S., Epstein, L. M., Timofeeva, T. V., Struchkov, Yu. T., Kreindlin, A. Z., Fadeeva, S. S. & Rybinskaya, M. I. (1991). *J. Organomet. Chem.* **401**, 133-143.
Shubina, E. S., Epstein, L. M., Yanovsky, Y. I., Timofeeva, T. V., Struchkov, Yu. T., Kreindlin, A. Z., Fadeeva, S. S. & Rybinskaya, M. I. (1988). *J. Organomet. Chem.* **345**, 313-320.
Spek, A. L. (1991). *PLATON. Molecular Geometry Program*. Univ. of Utrecht, The Netherlands.
Spek, A. L. (1991). *PLUTON. Molecular Graphics Program*. Univ. of Utrecht, The Netherlands.
Struchkov, Yu. T., Batsanov, A. S., Toma, S. & Salisova, M. (1987). *J. Organomet. Chem.* **329**, 375-379.
Yamakawa, K. & Hisatome, M. (1973). *J. Organomet. Chem.* **52**, 407-424.

Acta Cryst. (1994). C**50**, 23–25

Structure of (BEDT-TTF)$_4$[Hg$_2$Br$_6$].THF

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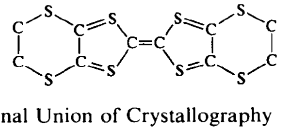
Abstract

The structure of tetrakis[3,4;3′4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalen]ium hexabromodimercurate tetrahydrofuran consists of two-dimensional sheets of BEDT-TTF separated by $Hg_2Br_6^{2-}$ anions and THF molecules centered at $x = 0$.

Comment

As a result of their unusual transport properties, salts of BEDT-TTF have attracted considerable attention (Williams *et al.*, 1987). Of particular interest are the organomineral salts, which show the highest superconducting transition temperatures in the BEDT-TTF family or in other organic salts. We report here the crystal structure of a newly synthesized salt, (BEDT-TTF)$_4$[Hg$_2$Br$_6$].THF.



The anion is different from that found in (BEDT-TTF)$_4$[HgBr$_4$].TCE (TCE = 1,1,2-trichloroethane) (Bu, Coppens & Naughton, 1990), but comparable to the Hg$_2$I$_6$ anion in (BEDT-TTF)$_4$[Hg$_2$I$_6$][I$_8$] (Bu & Coppens, 1992).

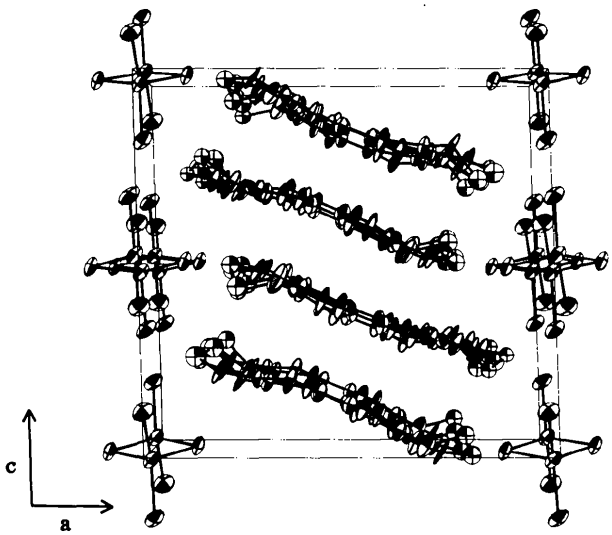


Fig. 1. The unit-cell packing diagram viewed along the *b* axis. Thermal ellipsoids are drawn at the 50% probability level. The THF molecule is omitted.

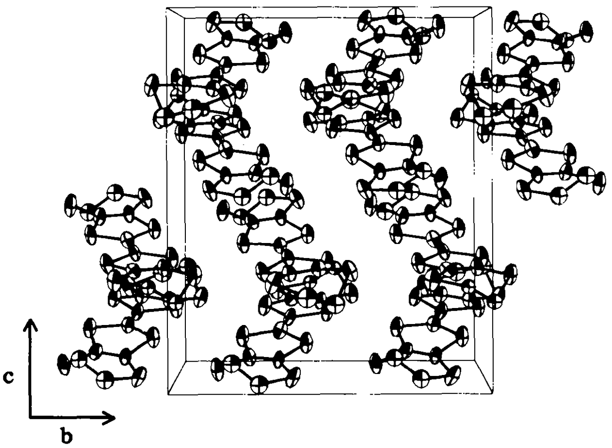


Fig. 2. The unit-cell packing diagram viewed along the *a* axis. Thermal ellipsoids are drawn at the 50% probability level. Only the BEDT-TTF molecules are shown.

Experimental

Crystal data

4C$_{10}$H$_8$S$_8$[Hg$_2$Br$_6$].-
C$_4$H$_8$O
M_r = 2491.3
Monoclinic
$P2_1/c$
a = 17.080 (2) Å
b = 13.467 (3) Å
c = 15.991 (4) Å

D_x = 2.25 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 17–19°
μ = 8.31 mm^{-1}
T = 293 K

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