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Hydrogen Bonding in Ferrocene Derivatives: Structures of 1-Ferrocenyl-2,2-dimethylpropan-1-ol and 2,2′-(1,1′-Ferrocenediyl)di(propan-2-ol)

Yiwei Li and George Ferguson

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Christopher Glidewell and Choudhury M. Zakaria

School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland

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Abstract

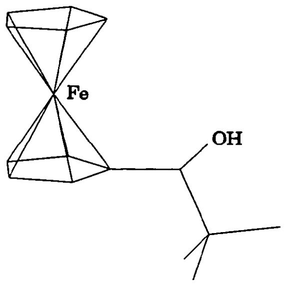
In 1-ferrocenyl-2,2-dimethylpropan-1-ol, [Fe(C_5H_5){(C_5H_4)CH(OH)^{t}Bu}] (I), the molecules are linked by hydrogen bonds to form ribbons around crystallographic 2_1 axes; the O···O distance in the hydrogen bonds is 2.802 (11) Å and the molecules are disordered with *R* and *S* enantiomers occupying common sites. The diol 2,2′-(1,1′-ferrocenediyl)di(propan-2-ol), [Fe{(C_5H_4)CMe$_2$OH}$_2$] (II), crystallizes as centrosymmetric dimeric aggregates containing fully ordered hydroxyl groups; the dimers are formed by hydrogen bonding, with O···O distances of 2.811 (2) and 2.841 (2) Å.

Comment

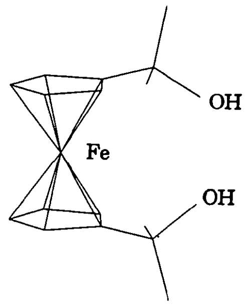
In α-ferrocenyl alcohols of type [(C_5H_5)Fe{(C_5H_4)C*R*′*R*″OH}] a wide range of O—H···O hydrogen bonding patterns occur in the solid state. Examples have been observed of centrosymmetric dimers containing four-membered (OH)$_2$ rings, as in Fc$_2$C(OH)CMe$_3$ [Fc = (C_5H_5)Fe(C_5H_4)] (Sharma, Cervantes-Lee & Pannell, 1992) and in FcCPh$_2$OH (Ferguson, Gallagher, Glidewell & Zakaria, 1993), of zigzag chains generated by the action of a glide plane, as in FcCH(OH)Ph (Ferguson, Gallagher, Glidewell & Zakaria, 1994*a*), and of systems with no hydrogen bonding at all, such as FcCMe(OH)Ph (Ferguson, Gallagher, Glidewell & Zakaria, 1993). The relationship between the hydrogen-bonding pattern and the steric and electronic nature of the substituents at the central C atom is, so far, obscure.

In ferrecenediols of type [Fe{(C_5H_4)C*R*′*R*″OH}$_2$], on the other hand, there is the possibility either that finite small aggregates may be formed as occurs in, for example, [(Me$_3$Si)C]PhSi(OH)$_2$ (Aiube, Buttrus, Eaborn, Hitchcock & Zora, 1985), or that chain formation can occur. Examples have been observed where diols form single-stranded chains, as in [(Me$_3$Si)$_2$N]$_2$Ge(OH)$_2$ (Glidewell, Hursthouse, Lloyd, Lumbard & Short, 1986), double-stranded chains, as in (^{t}Bu)$_2$Ge(OH)$_2$ (Puff, Franken, Schuh & Schwab, 1983), and threefold tubular chains, as in Ph$_2$Si(OH)$_2$ (Fawcett, Camerman & Camerman, 1977). However, the examples in the ferrocene series which have been examined so far, namely [Fe{(C_5H_4)CPh$_2$OH}$_2$] (Ferguson, Gallagher, Glidewell & Zakaria, 1993), and racemic [Fe{(C_5H_4)CPhMeOH}$_2$] and [Fe{(C_5H_4)CHMeOH}$_2$] (Ferguson, Gallagher, Glidewell & Zakaria, 1994*b*), have all been found to crystallize as dimers, containing eight-membered (OH)$_4$ rings.

Continuing our systematic study of hydrogen bonding in ferrocene derivatives, we now report the crystal and molecular structures of 1-ferrocenyl-2,2-dimethylpropan-1-ol, [(C_5H_5)Fe{(C_5H_4)CH(OH)^{t}Bu}] (I), and 2,2′-(1,1′-ferrocenediyl)di(propan-2-ol), [Fe{(C_5H_4)CMe$_2$OH}$_2$] (II).



(I)



(II)

Compound (I), Fig. 1, crystallizes in space group $P2_12_12_1$ which would normally accommodate either the *R* or the *S* form resulting from the chiral C atom adjacent to the ferrocenyl group. However, in the crystal structure, the hydroxyl group and the H atom bonded to this stereogenic C atom are disordered over two shared sites and hence both *R* and *S* forms are present. The site occupancies of the O atoms at the two sites consistently refined to 0.65 (1) and 0.35 (1); when the occupancies were constrained to be equal, the isotropic temperature factors attained unacceptable values. Hence, in the crystal selected for analysis there is an excess of one enantiomer over the other, and

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thus partial spontaneous resolution had occurred. Since the bulk sample is racemic, other crystals must exhibit enantiomeric excesses in the opposite sense. It is of course not necessary that all crystals have the same numerical value of the enantiomeric excess. The molecules form ribbons about a 2_1 axis parallel to the **a** direction (Fig. 2). Where hydrogen bonds form between neighbouring molecules the O···O distance is 2.802 (11) Å. The formation of such hydrogen bonds requires that a pair of *R* and *S* enantiomers are neighbours in order to achieve close approach of the O atoms. Neither molecule in such a pair can then form an O—H···O hydrogen bond with its other neighbour in the ribbon, and there may, indeed, be some molecules forming no hydrogen bonds at all. The best that can be achieved within a given ribbon is a pairwise coupling of the molecules giving sequences such as ...(*RS*)(*RS*)(*RS*)... or ...(*RS*)(*SR*)(*RS*)... *etc.*, where hydrogen bonds occur only within a bracketed pair. Hence it seems probable that in this compound, and possibly in other α-ferrocenyl monoalcohols also, the hydrogen-bonding scheme arises almost adventitiously in a crystal structure dominated by the packing of the large organic substituents, here ferrocenyl and *tert*-butyl.

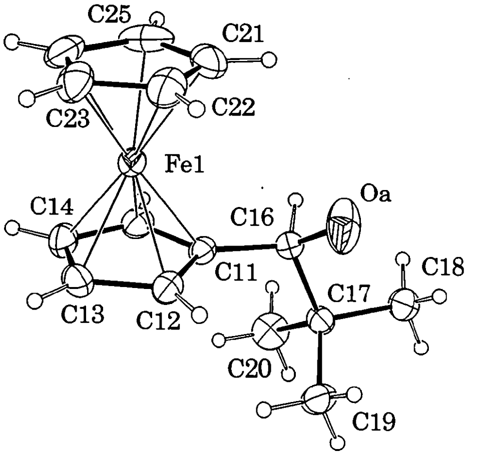

Fig. 1. A view of the [$(C_5H_5)Fe\{(C_5H_4)CH(OH)^tBu\}$] molecule (I) with our numbering scheme; non-H atoms are shown with displacement ellipsoids drawn at the 30% probability level and all H atoms are drawn as small spheres of arbitrary size.

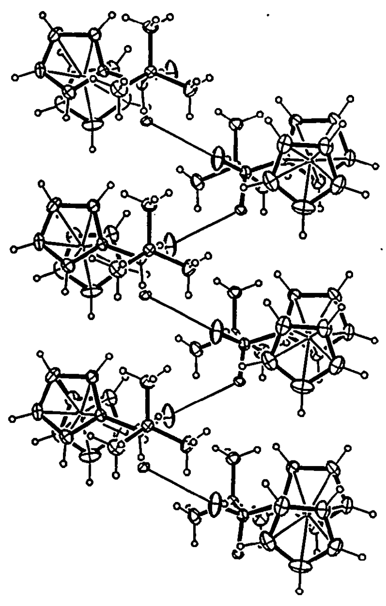

Fig. 2. A view of the hydrogen bonding in [$(C_5H_5)Fe\{(C_5H_4)$-$CH(OH)^tBu\}$].

Within the molecules of compound (I) the dimensions are largely typical of their types: the mean C—C distance in the substituted C_5 ring, 1.412 Å, exceeds that in the unsubstituted ring, 1.387 Å. The two C_5 rings are within 5° of an eclipsed conformation, as typically found for substituted ferrocenes.

Compound (II), [$Fe\{(C_5H_4)CMe_2OH\}_2$], crystallizes as centrosymmetric dimers, with the pairs of molecules linked by O—H···O hydrogen bonds forming an eight-membered ring, graph set $R^4_4(8)$, in which the hydroxyl H atoms are fully ordered (Fig. 3). In this respect it resembles [$Fe\{(C_5H_4)CHMeOH\}_2$], which forms similar centrosymmetric dimers with ordered hydroxyl H atoms (Ferguson, Gallagher, Glidewell & Zakaria, 1994*b*), but differs from [$Fe\{(C_5H_4)CPh_2OH\}_2$] and [$Fe\{(C_5H_4)CPhMeOH\}_2$], in both of which the dimer lies on a twofold rotation axis and where the hydroxyl H atoms are each disordered over two equally populated sites (Ferguson, Gallagher, Glidewell & Zakaria, 1993, 1994*b*). Within the dimeric aggregate of (II) the shortest O···O distances are 2.841 (2) (intramolecular) and 2.811 (2) Å (intermolecular), with corresponding O—H···O angles of 164 (2) and 168 (2)°, respectively. The mean C—C distance in the C_5 ring is 1.430 Å [*cf.* 1.412 Å for the substituted ring in compound (I)], and the C_5 rings are within 1.3° of a fully eclipsed conformation: as usual, the two substituents on the ferrocene nucleus are offset by $\frac{1}{5}$ turn.

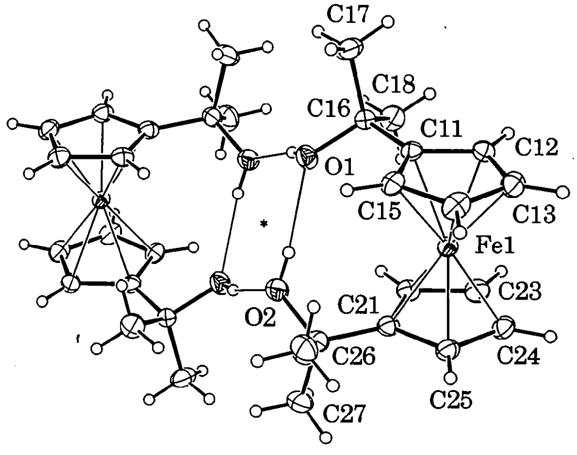

Fig. 3. A view of the [$Fe\{(C_5H_4)CMe_2OH\}_2]_2$ hydrogen-bonded dimer with our numbering scheme; non-H atoms are shown with displacement ellipsoids drawn at the 30% probability level and all H atoms are drawn as small spheres of arbitrary size.

Experimental

Crystals of compounds (I) and (II) were grown by slow evaporation of solutions in methanol and hexane, respectively.

Compound (I)

Crystal data

$[Fe(C_5H_5)(C_{10}H_{15}O)]$
$M_r = 272.17$
Orthorhombic
$P2_12_12_1$
$a = 5.9826\ (9)$ Å
$b = 10.1528\ (7)$ Å
$c = 21.785\ (3)$ Å
$V = 1323.2\ (3)$ Å^3
$Z = 4$
$D_x = 1.366$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10.0$–$12.5°$
$\mu = 1.12$ mm^{-1}
$T = 293$ K
Thin plate
$0.63 \times 0.22 \times 0.08$ mm
Pale yellow

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.668$, $T_{max} = 0.777$
1687 measured reflections
1687 independent reflections

1242 observed reflections $[I > 3.0\sigma(I)]$
$\theta_{max} = 26.9°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 27$
3 standard reflections
frequency: 60 min
intensity variation: 2.0%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.040$
$S = 0.99$
1242 reflections
163 parameters
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
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* (I)

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

	x	y	z	U_{eq}
Fe1	0.78297 (13)	0.47014 (7)	0.17058 (3)	0.0396 (4)
C11	0.7654 (9)	0.5157 (4)	0.07888 (19)	0.0353 (23)
C12	0.5486 (9)	0.5156 (6)	0.10601 (23)	0.048 (3)
C13	0.5450 (12)	0.6093 (6)	0.1542 (3)	0.057 (3)
C14	0.7571 (13)	0.6674 (5)	0.15700 (24)	0.054 (3)
C15	0.8922 (10)	0.6104 (5)	0.11121 (24)	0.047 (3)
C16	0.8432 (9)	0.4332 (5)	0.02611 (23)	0.040 (3)
C17	0.7949 (9)	0.4931 (5)	−0.03767 (21)	0.0386 (23)
C18	0.8924 (13)	0.4022 (6)	−0.0867 (3)	0.062 (4)
C19	0.5455 (10)	0.5081 (7)	−0.0472 (3)	0.056 (3)
C20	0.9054 (13)	0.6277 (6)	−0.0430 (3)	0.063 (4)
C21	0.9081 (15)	0.2852 (7)	0.1800 (3)	0.068 (4)
C22	0.7072 (14)	0.2927 (6)	0.2093 (3)	0.062 (4)
C23	0.7178 (13)	0.3899 (6)	0.25381 (25)	0.060 (4)
C24	0.9261 (13)	0.4441 (6)	0.2536 (3)	0.066 (4)
C25	1.0504 (12)	0.3782 (8)	0.2073 (4)	0.077 (5)
O*a*†	0.7676 (19)	0.3085 (5)	0.0280 (3)	0.087 (6)
O*b*	1.0600 (16)	0.3966 (10)	0.0364 (4)	0.036 (5)
*Cp*1‡	0.70166	0.58370	0.12145	
*Cp*2	0.86193	0.35802	0.22082	

† O*a* and O*b* are disordered with occupancies of 0.65 (1) and 0.35 (1), respectively.

‡ *Cp*1 and *Cp*2 are the centroids of the rings C11–C15 and C21–C25, respectively.

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

Fe1—C11	2.053 (4)	C12—C13	1.416 (8)
Fe1—C12	2.039 (5)	C13—C14	1.401 (10)
Fe1—C13	2.038 (6)	C14—C15	1.408 (9)
Fe1—C14	2.030 (5)	C16—C17	1.544 (7)
Fe1—C15	2.032 (5)	C16—O*a*	1.345 (8)
Fe1—C21	2.032 (6)	C16—O*b*	1.367 (10)
Fe1—C22	2.040 (5)	C17—C18	1.528 (8)
Fe1—C23	2.026 (5)	C17—C19	1.514 (8)
Fe1—C24	2.019 (6)	C17—C20	1.522 (8)
Fe1—C25	2.018 (6)	C21—C22	1.363 (11)
Fe1—*Cp*1	1.647	C21—C25	1.403 (13)
Fe1—*Cp*2	1.647	C22—C23	1.384 (9)
C11—C12	1.426 (8)	C23—C24	1.362 (11)
C11—C15	1.413 (7)	C24—C25	1.421 (11)
C11—C16	1.496 (7)	O*a*···O*b*^{i}	2.802 (11)
C12—C11—C15	106.4 (4)	O*a*—C16—O*b*	93.3 (7)
C12—C11—C16	127.0 (5)	C16—C17—C18	108.7 (4)
C15—C11—C16	126.6 (5)	C16—C17—C19	110.4 (4)
C11—C12—C13	108.7 (5)	C16—C17—C20	109.9 (4)
C12—C13—C14	107.6 (5)	C18—C17—C19	109.9 (5)
C13—C14—C15	108.4 (5)	C18—C17—C20	108.8 (5)
C11—C15—C14	108.9 (5)	C19—C17—C20	109.1 (5)
C11—C16—C17	114.4 (4)	C22—C21—C25	107.4 (6)
C11—C16—O*a*	113.5 (5)	C21—C22—C23	109.1 (7)
C11—C16—O*b*	108.8 (5)	C22—C23—C24	109.1 (6)
C17—C16—O*a*	109.6 (5)	C23—C24—C25	106.9 (6)
C17—C16—O*b*	115.6 (5)	C21—C25—C24	107.5 (6)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.

Compound (II)

Crystal data

$[Fe(C_8H_{11}O)_2]$
$M_r = 302.19$
Monoclinic
$P2_1/n$
$a = 7.1486\ (4)$ Å
$b = 12.4464\ (8)$ Å
$c = 16.4802\ (9)$ Å
$\beta = 97.609\ (4)°$
$V = 1453.40\ (15)$ Å^3
$Z = 4$

$D_x = 1.381$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 20.0$–$25.0°$
$\mu = 1.04$ mm^{-1}
$T = 293$ K
Pale yellow
$0.61 \times 0.55 \times 0.43$ mm
Block

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.961$, $T_{max} = 0.989$
4510 measured reflections
4215 independent reflections

3600 observed reflections $[I > 3.0\sigma(I)]$
$R_{int} = 0.026$
$\theta_{max} = 29.9°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity variation: 1.7%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.044$
$S = 1.64$
3600 reflections
180 parameters
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
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* (II)

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

	x	y	z	$U_{\rm eq}$
Fe1	0.249273 (20)	0.177563 (13)	0.004082 (9)	0.02744 (9)
O1	0.34518 (16)	0.42176 (8)	−0.09239 (6)	0.0410 (5)
O2	0.32422 (17)	0.45345 (8)	0.07687 (6)	0.0476 (6)
C11	0.22586 (18)	0.24555 (10)	−0.11051 (7)	0.0307 (5)
C12	0.24449 (20)	0.13119 (10)	−0.11557 (7)	0.0365 (6)
C13	0.09166 (22)	0.08288 (11)	−0.08049 (9)	0.0422 (6)
C14	−0.02105 (20)	0.16679 (11)	−0.05402 (9)	0.0417 (6)
C15	0.06015 (18)	0.26709 (10)	−0.07307 (8)	0.0349 (5)
C16	0.34627 (19)	0.32891 (9)	−0.14458 (7)	0.0321 (6)
C17	0.25440 (23)	0.35996 (13)	−0.23047 (8)	0.0493 (7)
C18	0.54527 (21)	0.29042 (12)	−0.14660 (9)	0.0456 (7)
C21	0.32029 (18)	0.26513 (10)	0.10900 (7)	0.0327 (5)
C22	0.48480 (18)	0.24023 (11)	0.07242 (8)	0.0353 (6)
C23	0.50001 (20)	0.12582 (11)	0.06670 (8)	0.0395 (6)
C24	0.34588 (21)	0.07987 (11)	0.10075 (8)	0.0399 (6)
C25	0.23500 (21)	0.16526 (10)	0.12697 (8)	0.0371 (6)
C26	0.25966 (22)	0.37587 (10)	0.13147 (8)	0.0396 (6)
C27	0.3601 (3)	0.40275 (13)	0.21666 (9)	0.0593 (10)
C28	0.0474 (3)	0.38581 (13)	0.12885 (11)	0.0579 (9)
*Cp*1†	0.12022	0.17870	−0.08673	
*Cp*2	0.37720	0.17526	0.09517	

†*Cp*1 and *Cp*2 are the centroids of the rings C11-C15 and C21-C25, respectively.

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

Fe1—C11	2.0559 (11)	C11—C15	1.4316 (19)
Fe1—C12	2.0506 (12)	C11—C16	1.5036 (18)
Fe1—C13	2.0457 (13)	C12—C13	1.4342 (21)
Fe1—C14	2.0443 (14)	C13—C14	1.4225 (22)
Fe1—C15	2.0569 (12)	C14—C15	1.4291 (19)
Fe1—C21	2.0501 (12)	C16—C17	1.5290 (17)
Fe1—C22	2.0517 (12)	C16—C18	1.5056 (20)
Fe1—C23	2.0500 (13)	C21—C22	1.4249 (19)
Fe1—C24	2.0499 (13)	C21—C25	1.4326 (18)
Fe1—C25	2.0469 (13)	C21—C26	1.5057 (18)
Fe1—*Cp*1	1.651	C22—C23	1.4322 (19)
Fe1—*Cp*2	1.651	C23—C24	1.4212 (21)
O1—C16	1.4412 (15)	C24—C25	1.4266 (21)
O1—H1	0.69 (2)	C26—C27	1.5270 (20)
O2—C26	1.4370 (16)	C26—C28	1.5175 (23)
O2—H2	0.80 (2)	O1···O2	2.8407 (15)
C11—C12	1.4330 (18)	O1···O2$^{\rm i}$	2.8113 (15)
C11—Fe1—C12	40.85 (5)	C22—C21—C25	107.24 (12)
C16—O1—H1	109.4 (17)	C22—C21—C26	125.71 (11)
C26—O2—H2	116.7 (13)	C25—C21—C26	126.81 (12)
C12—C11—C15	107.44 (11)	C21—C22—C23	108.56 (12)
C12—C11—C16	126.97 (12)	C22—C23—C24	107.73 (12)
C15—C11—C16	125.39 (11)	C23—C24—C25	108.10 (11)
C11—C12—C13	108.14 (12)	C21—C25—C24	108.37 (12)
C12—C13—C14	107.97 (11)	O2—C26—C21	109.53 (10)
C13—C14—C15	108.12 (13)	O2—C26—C27	106.11 (11)
C11—C15—C14	108.33 (12)	O2—C26—C28	109.28 (12)
O1—C16—C11	106.36 (10)	C21—C26—C27	108.12 (12)
O1—C16—C17	108.32 (10)	C21—C26—C28	112.76 (11)
O1—C16—C18	110.37 (11)	C27—C26—C28	110.81 (13)
C11—C16—C17	108.86 (11)	O1—H1···O2$^{\rm i}$	168 (2)
C11—C16—C18	112.21 (10)	O2—H2···O1	164 (2)
C17—C16—C18	110.57 (11)		

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

The space groups were determined unambiguously from the systematic absences [for (I), $P2_12_12_1$, $h00$ absent if $h = 2n + 1$, $0k0$ absent if $k = 2n + 1$, $00l$ absent if $l = 2n + 1$; for (II), $P2_1/n$, $h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$]. It became apparent during structure solution for (I) that the hydroxyl O atom was disordered over two sites, with occupancies of 0.65 (1) and 0.35 (1), from difference maps and isotropic refinement; all H atoms except for that of the disordered hydroxyl group were clearly visible in difference maps at intermediate stages of the refinement. The C—H H atoms were then positioned on geometric grounds (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations; no allowance was made for the disordered hydroxyl H atom. Although the bulk sample of (I) is racemic it crystallizes in a chiral space group; refinement (Rogers, 1981) with the opposite enantiomer system to that reported here, converged at higher R values ($R = 0.038$, $wR = 0.048$ compared with 0.032 and 0.040, respectively) showing that the model reported is the correct one for the crystal chosen. In the case of (II), all H atoms were clearly visible in difference maps at intermediate stages of the refinement. The C—H H atoms were then positioned on geometric grounds (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations; the hydroxyl H atoms were allowed to refine isotropically.

No solvent of crystallization was detected in the lattices and an examination of the crystal structures using *PLATON* (Spek, 1992) revealed no potential volume for any solvent molecules. Data collection and cell refinement was performed using *CAD*-4 *Software* (Enraf-Nonius, 1989). Data reduction, structure solution and refinement, and preparation of the material for publication were performed using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The diagrams were prepared using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*O*-Ethyl dithiocarbonato-κ*S*)phenylmercury, [Hg($C_3H_5OS_2$)(C_6H_5)]

Edward R. T. Tiekink

Department of Chemistry, The University of Adelaide, Adelaide, SA 5005, Australia

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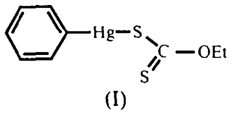
Abstract

The Hg atom in [PhHg(S_2COEt)] adopts a linear coordination geometry defined by the phenyl C atom [2.06 (1) Å] and an S atom [2.342 (3) Å] such that the C—Hg—S angle is 176.1 (4)°. A weak intramolecular Hg· · ·S contact of 3.209 (4) Å is noted.

Comment

The xanthate ligand (ROCS_2^-) is known to adopt a variety of coordination modes (Tiekink & Winter, 1992). For monodentate coordination *via* one of the S atoms, a structural variation may occur such that either the pendent S atom or the O atom may be directed towards the metal centre (Tiekink & Winter, 1992). The different conformations have been termed the *S,S* and *S,O* conformations, respectively. Recent studies on a series of triorganophosphinegold(I) xanthates have shown that both conformations may be found; these have been rationalized in terms of packing efficiency (Siasios & Tiekink, 1993*a*,*b*). While a similar variation of structure is possible for the organomercury xanthates, to date only the *S,S* conformation has been found. It was within the context of these studies that the structure of the title compound (I) was investigated.



(I)

The Hg atom in (I) adopts the expected linear coordination geometry, and is cooordinated by a phenyl C atom and the S(1) atom from a monodentate xanthate ligand. The second S atom is 3.209 (4) Å from the Hg atom. This latter contact is less than the sum of the van der Waals radii of Hg and S (3.3 Å; Bondi, 1964). The Hg—S(1)—C(1)—S(2) torsion angle is −9 (1)° and the dihedral angle between the planes through the phenyl ring and the S_2CO moiety is 15.3°. Other geometric parameters for the molecule are as expected. The closest intermolecular contact involving the non-H atoms, 3.476 (4) Å, occurs between Hg and S(1′) (symmetry operation: $1-x, -y, -z$).

The Hg-atom coordination geometry found in the title complex closely resembles those found in the related species [MeHg(S_2COMe)] (Tiekink, 1986), [PhHg(S_2COMe)] and [PhHg(S_2CO^iPr)] (Tiekink, 1987). Indeed, similar structures have been found for the related dithiocarbamate species [MeHg(S_2CNEt_2)] (Chieh & Leung, 1976) and [PhHg(S_2CNEt_2)] (Tiekink, 1987), where the conformational flexibility of the xanthate ligand is not available.

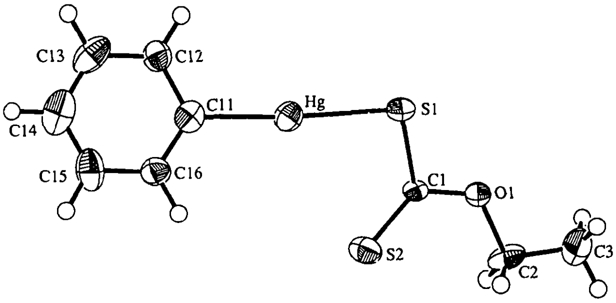


Fig. 1. Molecular structure of [PhHg(S_2COEt)] showing 50% probability displacement ellipsoids (Johnson, 1976).

Experimental

The title compound was prepared according to the method described in the literature (Tiekink, 1987). Crystals suitable for the X-ray analysis were grown by the vapour diffusion of diethyl ether into an acetonitrile solution of the compound (m.p. 394-395 K).

Crystal data

[Hg($C_3H_5OS_2$)(C_6H_5)]
$M_r = 398.9$
Orthorhombic
Pbca
$a = 11.14$ (1) Å
$b = 27.092$ (3) Å
$c = 7.179$ (4) Å
$V = 2166$ (2) Å^3
$Z = 8$
$D_x = 2.446$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 37.2\text{-}43.8°$
$\mu = 14.6$ mm^{-1}
$T = 293$ K
Needle
0.11 × 0.16 × 0.48 mm
Pale yellow