

[ZrF <sub>4</sub> (dmsO)(H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O				
S	0.49163 (6)	0.86829 (5)	0.13942 (4)	0.0265 (2)
F1	0.4827 (2)	0.3406 (2)	0.1566 (1)	0.0390 (9)
F2	0.2888 (2)	0.3887 (1)	0.3925 (1)	0.0407 (8)
F3	0.1903 (2)	-0.0055 (1)	0.0780 (1)	0.0384 (8)
F4	0.1623 (2)	0.0409 (2)	0.3763 (1)	0.046 (1)
O1	0.5011 (2)	0.0202 (2)	0.2603 (1)	0.0356 (9)
O2	0.5843 (2)	0.2977 (2)	0.4437 (2)	0.0381 (9)
O3	0.0568 (2)	0.2259 (2)	0.1546 (2)	0.042 (1)
O4	0.0636 (2)	0.7451 (2)	0.4741 (2)	0.039 (1)
O5	0.8918 (2)	0.4581 (2)	0.2272 (2)	0.048 (1)
C1	0.6967 (3)	0.8153 (3)	0.2116 (3)	0.050 (2)
C2	0.3011 (3)	0.6822 (3)	0.1562 (3)	0.046 (2)

Table 2. Selected bond distances (Å) and angles (°)

[Zr <sub>2</sub> F <sub>8</sub> (dmsO) <sub>4</sub> ]			
Zr—F2	1.967 (2)	S1—O1	1.537 (3)
Zr—F4	1.968 (2)	S1—C1	1.783 (4)
Zr—F3	1.992 (2)	S1—C2	1.784 (4)
Zr—F1 <sup>i</sup>	2.147 (2)	S2—O2	1.541 (3)
Zr—F1	2.163 (2)	S2—C4	1.780 (3)
Zr—O2	2.203 (2)	S2—C3	1.789 (5)
Zr—O1	2.204 (2)		
F2—Zr—F4	175.6 (1)	F3—Zr—O2	75.77 (9)
F2—Zr—F3	90.2 (1)	F3—Zr—O1	77.08 (9)
F2—Zr—F1 <sup>i</sup>	90.2 (1)	F1 <sup>i</sup> —Zr—F1	64.75 (8)
F2—Zr—F1	88.7 (1)	F1 <sup>i</sup> —Zr—O2	137.68 (8)
F2—Zr—O2	89.3 (1)	F1 <sup>i</sup> —Zr—O1	69.48 (9)
F2—Zr—O1	92.3 (1)	F1—Zr—O2	72.93 (8)
F4—Zr—F3	93.2 (1)	F1—Zr—O1	134.22 (9)
F4—Zr—F1 <sup>i</sup>	88.60 (9)	O2—Zr—O1	152.8 (1)
F4—Zr—F1	86.91 (9)	O1—S1—C1	105.2 (2)
F4—Zr—O2	88.8 (1)	O1—S1—C2	102.7 (2)
F4—Zr—O1	91.2 (1)	O2—S2—C4	106.2 (1)
F3—Zr—F1 <sup>i</sup>	146.55 (8)	O2—S2—C3	102.7 (2)
F3—Zr—F1	148.69 (8)		

[ZrF <sub>4</sub> (dmsO)(H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O			
Zr—F4	1.990 (1)	Zr—O3	2.218 (2)
Zr—F1	1.991 (1)	Zr—O2	2.221 (1)
Zr—F3	2.022 (1)	S—O1 <sup>ii</sup>	1.539 (1)
Zr—F2	2.039 (1)	S—C2	1.777 (2)
Zr—O1	2.180 (2)	S—C1	1.779 (3)
F4—Zr—F1	176.32 (5)	F3—Zr—O1	75.89 (5)
F4—Zr—F3	91.70 (5)	F3—Zr—O3	71.43 (5)
F4—Zr—F2	84.50 (5)	F3—Zr—O2	144.27 (6)
F4—Zr—O1	88.87 (6)	F2—Zr—O1	140.51 (4)
F4—Zr—O3	90.25 (6)	F2—Zr—O3	71.82 (5)
F4—Zr—O2	92.60 (5)	F2—Zr—O2	72.71 (5)
F1—Zr—F3	91.67 (5)	O1—Zr—O3	147.27 (5)
F1—Zr—F2	91.92 (5)	O1—Zr—O2	68.76 (5)
F1—Zr—O1	93.39 (5)	O3—Zr—O2	143.95 (6)
F1—Zr—O3	89.42 (6)	O1 <sup>ii</sup> —S—C2	105.8 (1)
F1—Zr—O2	85.52 (5)	O1 <sup>ii</sup> —S—C1	102.2 (1)
F3—Zr—F2	143.02 (5)	C2—S—C1	98.4 (1)

Symmetry codes: (i)  $1-x, 1-y, -z$ ; (ii)  $x, 1+y, z$ .

The compound [Zr<sub>2</sub>F<sub>8</sub>(dmsO)<sub>4</sub>] (I) was synthesized by recrystallization of ZrCl<sub>4</sub> in dmsO and subsequent fluorination by HF gas under a controlled atmosphere, or by recrystallization of ZrF<sub>4</sub> in dmsO as described by Muetterties (1960). The complex is hygroscopic. After addition of water to the ZrF<sub>4</sub> solution in dmsO at 423 K, (II) precipitates from the filtered solution at the ambient temperature; it is stable in air.

A small crystal of (I) was sealed in a 0.3 mm diameter Lindemann tube under a controlled atmosphere for the X-ray structure investigations. Stoe DIF4 software was used for data collection and cell refinement and Stoe REDU4 software for data reduction. The structure was solved and refined using SHELX76. SCHAKAL (Keller, 1989) was used for the molecular graphics.

The conditions limiting reflections led to the space groups P2<sub>1</sub>/n for (I) and P $\bar{1}$  for (II). Direct methods allowed the Zr

atoms to be located, other atoms were calculated from difference Fourier maps. The refinement used anisotropic thermal factors for all non-H atoms. The final atomic coordinates are listed in Table 1 while Table 2 gives the main interatomic distances in the two compounds.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55881 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1016]

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## Structure of Bis[chloro{1-[(4-chloro-2-hydroxyphenyl)iminomethyl]naphthalen-2-olato-O,O',N'}]iron(III)]

AYHAN ELMALI†

*Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstrasse 20, 6100 Darmstadt, Germany*

YALCIN ELERMAN

*Department of Engineering Physics, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey*

INGRID SVOBODA AND HARTMUT FUESS

*Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstrasse 20, 6100 Darmstadt, Germany*

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## Abstract

Two identical [FeLCI] [ $L = N$ -(4-chloro-2-hydroxyphenyl)-3-hydroxy-2-naphthaldimine] fragments, related by an inversion centre, are combined by the two bridging

† Permanent address: Department of Engineering Physics, Faculty of Sciences, University of Ankara, Besevler, Ankara, Turkey.

O atoms, forming a binuclear unit, dichlorobis- $\mu$ -{1-[4-chloro-(2-oxido-1:2 $\kappa^2$ O')-phenyliminomethyl]naphalen-2-olato}-1 $\kappa^2$ N,O;2 $\kappa^2$ N,O-diiron(III). The two iron(III) centres are 3.186 (4) Å apart and the distance between the two bridging O atoms amounts to 2.417 (8) Å. The two Fe—O distances [Fe—O(2) and Fe—O(2A)] are different [2.047 (8) and 1.951 (8) Å, respectively]. The Fe—O(2)—Fe(A) angle in the central four-membered ring is 105.64 (4)°.

### Comment

The title compound was prepared by the reaction between 2-hydroxynaphthalene-1-carbaldehyde and 2-amino-4-chlorophenol in acetonitrile solution. To this solution was added a stoichiometric amount of FeCl<sub>2</sub>·4H<sub>2</sub>O in methanol solution. The mixture was refluxed for 3 h. Dark brown crystals were formed during the reflux operation. The magnetic properties of dimeric iron(III) complexes with Schiff bases have been studied extensively (Kurtz, 1990). Susceptibility measurement of the title compound in the temperature range 4.2 < T < 286 K revealed anti-ferromagnetic coupling (J = -10.9). A detailed discussion of the magnetic properties and their relation to the crystal structures of the title compound and some other substances is in preparation (Elmali *et al.*, 1993).

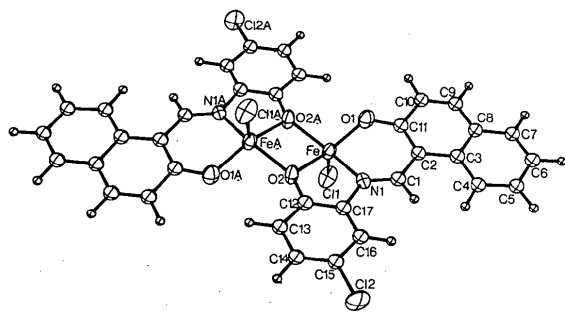


Fig. 1. The molecular structure of the title compound. Anisotropic ellipsoids represent 50% probability boundaries. C and H atoms are represented by spheres of arbitrary radii.

### Experimental

#### Crystal data

[Fe<sub>2</sub>Cl<sub>2</sub>(C<sub>17</sub>H<sub>10</sub>ClNO<sub>2</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 774.05

Monoclinic

*P*<sub>2</sub>/c

*a* = 7.960 (1) Å

*b* = 20.467 (2) Å

*c* = 11.565 (1) Å

β = 125.06 (1)°

*V* = 1542.3 (4) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.666 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 1.98–11.26°

μ = 1.332 mm<sup>-1</sup>

*T* = 301 K

Prism

0.2 × 0.1 × 0.025 mm

Dark brown

#### Data collection

Enraf–Nonius CAD-4 diffractometer

ω-2θ scans

Absorption correction: empirical

*T<sub>min</sub>* = 0.683, *T<sub>max</sub>* = 0.999

2973 measured reflections

1620 independent reflections

869 observed reflections  
[*F* < 4.0σ(*F*)]

*R<sub>int</sub>* = 0.058

θ<sub>max</sub> = 23°

*h* = -8 → 8

*k* = 0 → 22

*l* = -12 → 12

3 standard reflections

frequency: 120 min

intensity variation: 2%

#### Refinement

Refinement on *F*

Final *R* = 0.0685

*wR* = 0.0489

869 reflections

124 parameters

*w* = 2.6866/[σ<sup>2</sup>(*F*) + 0.0*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.03

Δρ<sub>max</sub> = 0.54 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.62 e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Data collection: *Enraf–Nonius Structure Determination Package* (Frenz, 1985). Cell refinement: *Enraf–Nonius Structure Determination Package*. Data reduction: *Enraf–Nonius Structure Determination Package*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL76* (Sheldrick, 1976).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Fe	0.0899 (4)	0.5439 (1)	0.6373 (2)	0.037 (1)
Cl(1)	0.3547 (7)	0.6042 (2)	0.6915 (4)	0.058 (2)
N	0.1978 (17)	0.4872 (5)	0.8137 (10)	0.027 (6)
C(1)	0.2093 (21)	0.5048 (6)	0.9230 (13)	0.029 (4)
C(2)	0.1251 (21)	0.5626 (5)	0.9372 (11)	0.025 (4)
C(3)	0.1634 (21)	0.5776 (6)	1.0707 (12)	0.034 (4)
C(4)	0.2854 (20)	0.5424 (7)	1.1939 (11)	0.035 (3)
C(5)	0.3200 (20)	0.5605 (6)	1.3208 (12)	0.044 (4)
C(6)	0.2318 (22)	0.6165 (6)	1.3309 (13)	0.043 (4)
C(7)	0.1118 (23)	0.6527 (7)	1.2138 (13)	0.048 (4)
C(8)	0.0713 (23)	0.6369 (6)	1.0825 (13)	0.040 (4)
C(9)	-0.0581 (22)	0.6734 (6)	0.9601 (13)	0.050 (5)
C(10)	-0.1033 (24)	0.6580 (6)	0.8320 (13)	0.046 (4)
C(11)	-0.0076 (23)	0.6006 (7)	0.8200 (13)	0.041 (4)
O(1)	-0.0614 (14)	0.5897 (4)	0.6903 (8)	0.049 (6)
O(2)	0.1146 (14)	0.4552 (4)	0.5668 (7)	0.041 (5)
C(12)	0.2256 (21)	0.4107 (6)	0.6708 (12)	0.026 (3)
C(13)	0.2878 (22)	0.3524 (6)	0.6432 (13)	0.042 (4)
C(14)	0.3993 (22)	0.3082 (6)	0.7560 (13)	0.039 (4)
C(15)	0.4417 (23)	0.3211 (6)	0.8863 (13)	0.035 (4)
Cl(2)	0.5672 (8)	0.2641 (2)	1.0188 (4)	0.063 (2)
C(16)	0.3811 (21)	0.3800 (6)	0.9122 (12)	0.028 (4)
C(17)	0.2719 (21)	0.4240 (6)	0.8029 (12)	0.025 (4)

Table 2. Geometric parameters (Å, °)

Fe—Cl(1)	2.200 (5)	Fe—O(2)	2.047 (8)
Fe—N	2.058 (9)	Fe—O(2A)	1.951 (8)
Fe—O(1)	1.884 (9)		
Fe—O(2)—Fe(A)	105.64 (3)	Cl(1)—Fe—O(2A)	109.64 (3)
N—Fe—Cl(1)	104.4 (3)	O(2)—Fe—N	79.2 (3)
O(1)—Fe—Cl(1)	108.4 (3)	N(1)—Fe—O(2A)	141.94 (3)
O(1)—Fe—N	86.5 (4)	O(2)—Fe—O(1)	142.8 (4)
O(2)—Fe—Cl(1)	108.4 (3)	O(1)—Fe—O(2A)	98.28 (4)

The structure was determined by direct methods and refined by anisotropic full-matrix least squares on  $F$ . All C atoms were refined isotropically. All H atoms were located geometrically (C—H distance 0.98 Å) and not refined.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55836 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1022]

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## Structures of 1-Ferrocenyl-1-phenylethanol, Ferrocenyl(diphenyl)methanol and Ferrocene-1,1'-diylbis(diphenylmethanol)

GEORGE FERGUSON AND JOHN F. GALLAGHER

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

CHRISTOPHER GLIDEWELL AND CHOUDHURY M. ZAKARIA

*Chemistry Department, The University, St. Andrews, Fife KY16 9ST, Scotland*

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## Abstract

Racemic 1-ferrocenyl-1-phenylethanol, [(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>)]CPhMeOH (I), crystallizes as discrete molecules which are not involved in hydrogen bonding; the shortest intermolecular O···O contact is 3.768(3) Å and the hydroxyl H atom is orientated towards the unsubstituted cyclopentadienyl ring. Ferrocenyl(diphenyl)methanol, [(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>)]CPh<sub>2</sub>OH (II) is hydrogen bonded to form centrosymmetric dimers with O···O 2.816(1) and H···O 2.52 Å. Ferrocene-1,1'-diylbis(diphenylmethanol), Fe[(C<sub>5</sub>H<sub>4</sub>)C(Ph)<sub>2</sub>COH]<sub>2</sub> (III) crystallizes as a dimeric aggregate with the Fe atoms on twofold crystallographic symmetry axes and the four O atoms defin-

ing a folded trapezium with O···O 2.762(2), 2.714(2) and 2.865(2) Å. The four hydroxyl groups are disordered equally over two orientations such that there are two half-occupancy H-atom sites between each hydrogen-bonded oxygen pair.

## Comment

Triphenylmethanol, Ph<sub>3</sub>COH, crystallizes as hydrogen-bonded tetrameric aggregates with threefold crystallographic symmetry, each containing an approximately tetrahedral arrangement of O atoms with necessarily disordered hydroxyl H atoms (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992). These aggregates are significantly different from the cyclic tetrameric aggregates found in triphenylsilanol, Ph<sub>3</sub>SiOH (Puff, Braun & Reuter, 1991), and in triphenylgermanol, Ph<sub>3</sub>GeOH (Ferguson, Gallagher, Murphy, Spalding, Glidewell & Holden, 1992), whose graph set (Etter, MacDonald & Bernstein, 1990) is  $R_4^4(8)$ . Triphenylmethanol can act as a host towards guest molecules such as methanol and dimethyl sulfoxide (Weber, Skobridis & Goldberg, 1989) albeit with hydrogen-bonding arrangements wholly different from that in unsolvated Ph<sub>3</sub>COH. The diol *m*-bis(diphenylhydroxymethyl)benzene, which forms similar host/guest aggregates with a range of different guest species, crystallizes as centrosymmetric dimers (Toda, Kai, Toyotaka, Yip & Mak, 1989) with graph set  $R_2^2(16)$ .

In order to assess the effect on the hydrogen-bonding patterns in the crystal lattice in alcohols of this general type by altering the steric demands at the central C atom, we have now determined the structures of racemic 1-ferrocenyl-1-phenylethanol, [(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>)]CPhMeOH (I); ferrocenyl(diphenyl)methanol, [(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>)]CPh<sub>2</sub>OH (II); and ferrocene-1,1'-diylbis(diphenylmethanol), Fe[(C<sub>5</sub>H<sub>4</sub>)C(Ph)<sub>2</sub>COH]<sub>2</sub> (III).

