

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.032$   
 $wR(F^2) = 0.087$   
 $S = 1.065$   
 6246 reflections  
 373 parameters  
 Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.004$   
 $\Delta\rho_{\max} = 0.406 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.620 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cu1—N3	1.9401 (17)	Cu2—N2	1.9417 (17)
Cu1—O4	1.9620 (15)	Cu2—O3	1.9728 (15)
Cu1—N1	1.975 (2)	Cu2—N4	1.9870 (18)
Cu1—O1	1.9888 (15)	Cu2—O2'	2.0146 (14)
Cu1—O6	2.6188 (15)	Cu2—O6'	2.4380 (15)
N3—Cu1—O4	85.16 (7)	O3—Cu2—N4	159.27 (8)
N3—Cu1—N1	96.03 (8)	N2—Cu2—O2'	171.77 (6)
O4—Cu1—N1	172.20 (8)	O3—Cu2—O2'	88.55 (6)
N3—Cu1—O1	174.32 (7)	N4—Cu2—O2'	93.26 (7)
O4—Cu1—O1	89.20 (6)	N2—Cu2—O6'	98.06 (6)
N1—Cu1—O1	89.48 (8)	O3—Cu2—O6'	106.94 (6)
N2—Cu2—O3	84.64 (6)	N4—Cu2—O6'	93.68 (7)
N2—Cu2—N4	94.75 (7)	O2'—Cu2—O6'	79.49 (5)

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

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O8—H108 <sup>i</sup> ...O7	0.78 (4)	1.95 (4)	2.700 (3)	160 (4)
O8 <sup>i</sup> —H2O8 <sup>i</sup> ...O1	0.69 (4)	2.16 (4)	2.803 (2)	156 (5)
O9 <sup>ii</sup> —H2O9 <sup>ii</sup> ...O5	0.66 (4)	2.23 (4)	2.867 (3)	162 (5)
O9—H1O9...O8 <sup>iii</sup>	0.75 (4)	1.99 (4)	2.726 (3)	164 (4)
N1—H2N1...O9 <sup>iv</sup>	0.83 (3)	2.15 (3)	2.979 (3)	176 (3)
N1—H1N1...O9	0.78 (3)	2.41 (3)	3.114 (3)	150 (3)
N4 <sup>v</sup> —H2N4 <sup>v</sup> ...O8 <sup>vi</sup>	0.82 (3)	2.40 (3)	3.107 (3)	144 (2)
N4—H1N4...O5 <sup>vii</sup>	0.83 (3)	2.25 (3)	3.074 (2)	173 (3)

Symmetry codes: (i)  $2 - x, -y, 2 - z$ ; (ii)  $1 - x, 1 - y, 2 - z$ ; (iii)  $x - 1, y, z$ ; (iv)  $1 - x, -y, 2 - z$ ; (v)  $1 - x, 1 - y, 1 - z$ ; (vi)  $x, y, z - 1$ .

All H atoms were located in  $\Delta F$  maps, were refined isotropically and assigned isotropic displacement parameters  $U(H) = 1.5U_{\text{eq}}(C \text{ or } N)$ .

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL97*.

We are grateful to the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Italy, for grants, to the Centro Interdipartimentale di Calcolo Automatico ed Informatica Applicata (CICAIA) of Modena University for computer facilities, and to the Centro Interdipartimentale Grandi Strumenti of Modena University for intensity data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1319). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Burla, M. C., Camalli, G., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.  
 Cornia, A. (1995). PhD thesis, University of Modena, Italy.  
 Cornia, A., Fabretti, A. C., Ferraro, F., Gatteschi, D. & Giusti, A. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3363–3366, and references therein.  
 Enraf-Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.  
 Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.  
 Fabretti, A. C., Giusti, A., Albano, V. G., Castellari, C., Gatteschi, D. & Sessoli, R. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2133–2137.  
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

*Acta Cryst.* (1999). **C55**, 2045–2047

**[(2*S*,4*S*)-4-Hydroxymethyl-1,3-dioxan-2-yl]-ferrocene**

JEROME CHIFFRE, ERIC MANOURY, JEAN-CLAUDE DARAN AND GILBERT G. A. BALAVOINE

*Laboratoire de Chimie de Coordination, UPR-CNRS 8241, 205 Route de Narbonne, 31077 Toulouse CEDEX, France. E-mail: daran@lcc-toulouse.fr*

(Received 6 July 1999; accepted 20 September 1999)

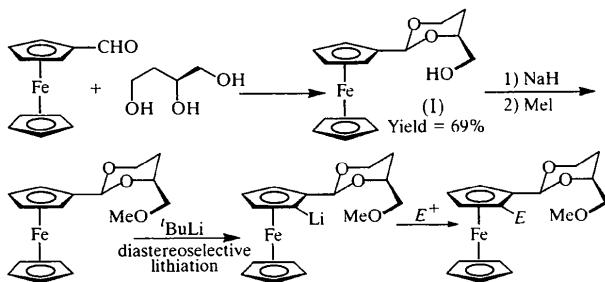
## Abstract

The structure of the title complex,  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{10}\text{H}_{13}\text{O}_3)]$ , shows the occurrence of two stereogenic centres in the hydroxymethyl-1,3-dioxane fragment. The *S* configuration found for these chiral C atoms agrees with the synthetic route. The dioxane ring has a nearly perfect chair conformation. O—H...O hydrogen bonds result in the formation of an eight-membered ring built from the arrangement of four complex molecules around a fourfold axis.

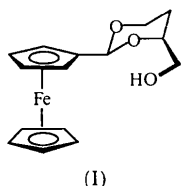
## Comment

For many years, owing to their involvement in numerous fields (catalysis, materials *etc.*; Togni & Hayashi, 1995), ferrocene derivatives have continued to create growing interest. Some of these applications require the use of chiral enantiomerically pure compounds, so much effort has been devoted to finding an efficient way to obtain these molecules (Batelle *et al.*, 1973; Ganter & Wagner, 1995; Riant *et al.*, 1993; Rebière *et al.*, 1993; Sammakia & Latham, 1996; Tsukazaki *et al.*, 1996). The title compound, [(2*S*,4*S*)-4-hydroxymethyl-

1,3-dioxan-2-yl]ferrocene, (I), is a direct precursor of [(2*S*,4*S*)-4-methoxymethyl-1,3-dioxan-2-yl]ferrocene which is the starting point for the efficient synthesis of various enantiomerically pure 2-substituted ferrocene-carbaldehydes (Riant *et al.*, 1993). Compound (I) was obtained from ferrocenecarboxaldehyde and (*S*)-1,2,4-butanetriol in 69% yield. During the synthesis, a new stereogenic centre is created, namely the asymmetrical carbon in the 2 position of the acetal ring. In order to confirm the structure of this new ferrocene derivative, we present here its X-ray analysis.



The molecular structure of (I) is shown in Fig. 1 with the atom-labelling scheme. As indicated by examination of the torsion angles in Table 1, the 1,3-dioxane ring has a chair conformation. As expected from the synthetic route, the hydroxymethyl dioxane fragment presents two stereogenic centres, C11 and C12. The C12 carbon



retains the *S* configuration initially present in (*S*)-1,2,4-butanetriol, whereas the newly created chiral C11 atom has an *S* configuration, thus confirming the proposition of Riant *et al.* (1993). It is worth pointing out that the hydroxymethyl side chain of the dioxane ring is oriented towards the C5 atom which is the carbon selectively attacked by the base during the stereoselective lithiation (see reaction scheme above). The H atom of the OH group is engaged in hydrogen bonding with the O atom

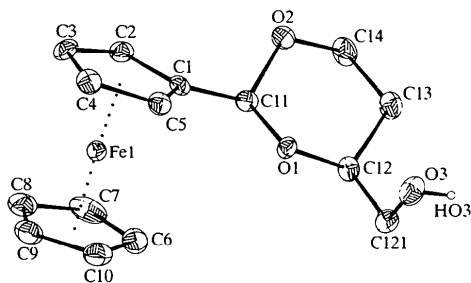


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms except that of the OH group have been omitted for clarity.

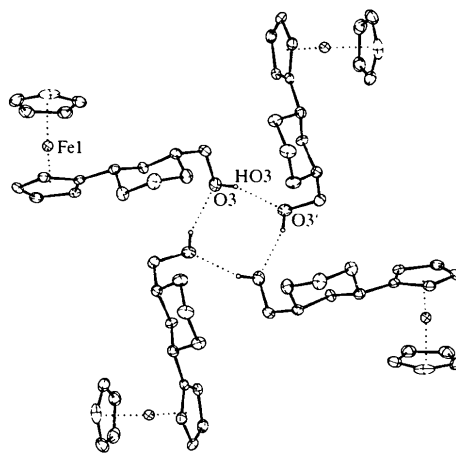


Fig. 2. Projection along *c* showing the arrangement of four molecules around the fourfold axis and hydrogen-bonding interactions.

of the OH group of the symmetry-related molecule, leading to an arrangement of four complexes around the fourfold axis, as shown in Fig. 2.

## Experimental

The title compound was synthesized according to the procedure of Riant *et al.* (1993) (see reaction scheme). Crystals were obtained by slow diffusion of hexane into a dichloromethane solution of [(2*S*,4*S*)-4-hydroxymethyl-1,3-dioxan-2-yl]ferrocene

### Crystal data

[Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>10</sub>H<sub>13</sub>O<sub>3</sub>)]

*M<sub>r</sub>* = 302.18

Tetragonal

*I*4

*a* = 20.521 (3) Å

*c* = 6.1384 (7) Å

*V* = 2584.8 (5) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.553 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 5000 reflections

θ = 1.98–24.25°

μ = 1.167 mm<sup>-1</sup>

*T* = 180 (2) K

Needle

0.853 × 0.243 × 0.116 mm

Yellow

### Data collection

Stoe IPDS diffractometer

φ scans

Absorption correction:

numerical (*X-SHAPE*;

Stoe, 1996a)

*T<sub>min</sub>* = 0.632, *T<sub>max</sub>* = 0.852

10 394 measured reflections

1100 independent reflections

(plus 914 Friedel-related

reflections)

1940 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.041

θ<sub>max</sub> = 24.25°

*h* = −23 → 23

*k* = −23 → 23

*l* = −7 → 7

200 standard reflections

frequency: 7 min

intensity decay: <0.5%

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.024

w*R*(*F*<sup>2</sup>) = 0.066

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.29 e Å<sup>-3</sup>

Δρ<sub>min</sub> = −0.22 e Å<sup>-3</sup>

$S = 1.133$   
 2054 reflections  
 172 parameters  
 H atoms treated by a  
 mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 3.7035P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)  
 Absolute structure:  
 Flack (1983)  
 Flack parameter =  $-0.01$  (2)

Tsukazaki, M., Tinkl, M., Roglans, A., Chapell, B. J., Taylor, N. J. & Snieckus, V. (1996). *J. Am. Chem. Soc.* **118**, 685.  
 Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

*Acta Cryst.* (1999). **C55**, 2047–2049

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C11	1.412 (3)	C1—C11	1.486 (4)
O1—C12	1.450 (3)	C12—C121	1.500 (4)
O2—C11	1.413 (3)	C12—C13	1.510 (4)
O2—C14	1.435 (4)	C13—C14	1.513 (4)
O3—C121	1.427 (4)		
C11—O1—C12	110.3 (2)	O1—C12—C121	107.9 (2)
C11—O2—C14	109.5 (2)	O1—C12—C13	109.2 (2)
C2—C1—C11	124.6 (3)	C121—C12—C13	114.9 (3)
C5—C1—C11	127.6 (3)	C12—C13—C14	110.5 (3)
O1—C11—O2	111.2 (2)	O2—C14—C13	110.8 (2)
O1—C11—C1	110.1 (2)	O3—C121—C12	111.9 (2)
O2—C11—C1	109.5 (2)		
C11—O1—C12—C13	57.5 (3)	C13—C14—O2—C11	-56.9 (3)
O1—C12—C13—C14	-51.1 (3)	C14—O2—C11—O1	64.1 (3)
C12—C13—C14—O2	51.6 (4)	O2—C11—O1—C12	-65.1 (3)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O3 <sup>i</sup>	0.76	2.01	2.720 (3)	156

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

The assignment of absolute configuration was confirmed by a Flack (1983) parameter of  $-0.01$  (2) from the final refinement.

Data collection: *IPDS Manual* (Stoe, 1996b). Cell refinement: *IPDS Manual*. Data reduction: *X-RED* (Stoe, 1996c). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *CAMERON* (Watkin *et al.*, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1052). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.  
 Batelle, L. E., Bau, R., Gokel, G. & Ugi, I. (1973). *J. Am. Chem. Soc.* **95**, 482–486.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Ganter, C. & Wagner, T. (1995). *Chem. Ber.* **128**, 1157–1161.  
 Rebière, F., Riant, O., Ricard, L. & Kagan, H. B. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 568–570.  
 Riant, O., Samuel, O. & Kagan, H. B. (1993). *J. Am. Chem. Soc.* **115**, 5835–5836.  
 Sammakia, T. & Latham, H. A. (1996). *J. Org. Chem.* **61**, 1629–1635.  
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Stoe (1996a). *X-SHAPE. Crystal Optimization for Numerical Absorption Correction*. Revision 1.01. Stoe & Cie, Darmstadt, Germany.  
 Stoe (1996b). *IPDS Manual*. Version 2.75. Stoe & Cie, Darmstadt, Germany.  
 Stoe (1996c). *X-RED. Data Reduction for Stadi-4 and IPDS*. Revision 1.08. Stoe & Cie, Darmstadt, Germany.  
 Togni, A. & Hayashi, T. (1995). In *Ferrocenes*. Weinheim: VCH.

## A long-chain alkyl-tethered $\text{Mo}_2\text{S}_2$ core, $[\text{Bu}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(n\text{-C}_6\text{H}_{13}\text{S})_2]$

QIANG WEI, BOTAO ZHUANG\* AND JIUTONG CHEN

*Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, People's Republic of China. E-mail: zbt@ms.fjirsm.ac.cn*

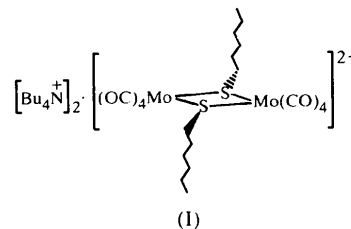
(Received 9 April 1999; accepted 27 August 1999)

## Abstract

The title compound, bis(tetrabutylammonium) bis( $\mu$ -hexanethiolato-*S:S*) bis [tetracarbonylmolybdenum(0)],  $(\text{C}_{16}\text{H}_{36}\text{N})_2[\text{Mo}_2(\text{C}_6\text{H}_{13}\text{S})_2(\text{CO})_8]$ , contains two  $\text{Bu}_4\text{N}^+$  cations and a centrosymmetric  $[\text{Mo}_2(\text{CO})_8(n\text{-C}_6\text{H}_{13}\text{S})_2]^{2-}$  anion. The structure of the anion can be viewed as a planar  $\text{Mo}_2\text{S}_2$  unit tethered by two long alkyl chains.

## Comment

Since 1984 low-valent dinuclear molybdenum thiolate complexes containing the  $\text{Mo}_2\text{S}_2$  unit and having two-electron transfer character, *e.g.*  $[\text{Mo}_2(\text{CO})_8(\text{SR})_2]^{2-}$  ( $R = \text{Ph}, \text{tBu}$ ), have been synthesized (Zhuang *et al.*, 1984; Smith *et al.*, 1987). Different  $R$  groups have been introduced into the  $\text{Mo}_2\text{S}_2$  unit, such as *m*-tolyl (Zhuang *et al.*, 1996), *p*-tolyl,  $\text{EtCO}_2\text{CH}_2$  (Zhuang *et al.*, 1986), to investigate the effect of the  $R$  group on the  $\text{Mo}_2\text{S}_2$  unit. The effects of long-chain purely alkyl  $R$  groups have interested us recently and the structure of the title compound, (I), which contains the *n*-hexyl  $[\text{CH}_3(\text{CH}_2)_4\text{CH}_2-]$  group, has been determined.



Compound (I) (Fig. 1) consists of three discrete structure fragments, namely two  $\text{Bu}_4\text{N}^+$  cations and the dianion  $[\text{Mo}_2(\text{CO})_8(n\text{-C}_6\text{H}_{13}\text{S})_2]^{2-}$ . The dianion comprises two equivalent Mo atoms, each of which is coordinated by four terminal carbonyls and two bridging *n*-hexane-