

## The crystal structure of 1,1'-(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane-7,16-diyldicarbonyl)ferrocene dihydrate

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### Abstract

The crystal and molecular structure of 1,1'-(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane-7,16-diyldicarbonyl)ferrocene have been determined. The crystal system is monoclinic,  $a$  8.761(17),  $b$  21.326(18),  $c$  13.250(8) Å,  $\beta$  95.56(10)° and space group  $P2_1/n$ . There are two molecules of water for each molecule of the title compound situated outside the cryptand ring system.

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The construction of redox-active host molecules by the incorporation of metallocene and quinone redox centres into crown ether and cryptand structural frameworks has received considerable recent attention in the chemical literature [1–5]. Some of these compounds have been shown to be selective [6,7] and redox-responsive [8,9] to the host binding of Group 1A metal guest cations in close proximity to the redox-active centre. Only a few structural characterisations have been reported on these types of host molecules [10–12] and to our knowledge this paper reports the first example of a crystal structure determination of a ferrocene cryptand.

### Experimental

#### *Synthesis*

The 1,1'-(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane-7,16-diyldicarbonyl)ferrocene was prepared by a published procedure [13], m.p. 183–184°C (lit. [13] 183–184°C).

Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a dilute diethyl ether solution of the title compound in the presence of water vapour.

#### *X-ray structure analysis*

Cell dimensions and reflection intensities were measured with graphite-monochromated Mo- $K_\alpha$  radiation on an Enraf–Nonius CAD-4 diffractometer from an irregular-shaped crystal of approximate size 0.5 × 0.3 × 0.3 mm. Three standard

Table 1

Fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses

	x	y	z		x	y	z
Fe	-461(2)	698(1)	1903(1)	C(8)	-226(12)	1432(5)	5436(8)
C(1)	-1582(12)	581(6)	3175(8)	C(9)	279(11)	2501(5)	5878(8)
C(2)	-2447(12)	353(6)	2309(9)	C(10)	-200(12)	3147(6)	5632(8)
C(3)	-1701(14)	-132(6)	1846(10)	C(11)	-1352(11)	3148(5)	3932(8)
C(4)	-268(12)	-201(5)	2436(8)	C(12)	-999(11)	3213(5)	2836(8)
C(5)	-175(12)	241(5)	3246(7)	O(2)	-788(7)	2044(4)	5428(5)
C(1')	1273(10)	1321(5)	1846(8)	O(3)	-36(8)	3307(4)	4600(5)
C(2')	1355(11)	863(6)	1094(9)	C(14)	2994(12)	680(5)	5292(8)
C(3')	-51(13)	891(5)	449(8)	C(15)	4365(11)	917(6)	4805(9)
C(4')	-954(11)	1347(5)	799(7)	C(16)	5215(10)	1865(6)	4051(8)
C(5')	-207(10)	1642(5)	1685(7)	C(17)	4624(11)	2488(6)	3773(8)
C(6)	1243(13)	252(5)	3970(8)	C(18)	2639(10)	2996(5)	2770(8)
C(13)	-879(12)	2154(5)	2239(7)	C(19)	1294(10)	2878(5)	1988(7)
O(1)	2094(9)	-204(4)	3967(6)	O(5)	4203(7)	1574(4)	4693(6)
O(4)	-2184(7)	2074(4)	2472(6)	O(6)	3252(7)	2416(4)	3114(5)
N(1)	1563(9)	726(4)	4613(6)	O(7)	931(12)	4584(5)	4473(7)
N(2)	-132(8)	2694(4)	2446(6)	O(8)	4226(13)	-351(6)	2660(9)
C(7)	773(12)	1342(5)	4570(7)				

reflections measured every 2 h showed a 3% drop in intensity during the period of data collection and correction factors were applied. The scan range of the  $\omega/2\theta$  scans was calculated from  $\omega = (1.3 + 0.35 \tan \theta)^\circ$  and the scan speed varied from 1.25 to 3.3° min<sup>-1</sup> depending on the intensity. 4395 unique reflections were measured within the range  $\theta$  2–25°. Of these, 2437 with  $I > 3\sigma(I)$  were considered observed and used in the analysis.

#### Crystal data

$C_{24}H_{32}N_2O_6Fe \cdot 2H_2O$ ,  $M_r = 536.4$ , monoclinic, space group  $P2_1/n$ ,  $a$  8.761(17),  $b$  21.326(18),  $c$  13.250(8) Å,  $\beta$  95.56(10)°,  $U$  2464 Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  1.446 g cm<sup>-3</sup>,  $F(000) = 1136$ , Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å,  $\mu$  0.670 mm<sup>-1</sup>. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic temperature factors and then anisotropically. Hydrogen atoms were included in calculated positions, "riding" on their respective carbon atoms with an isotropic temperature factor  $U$  0.07 Å<sup>2</sup>. The calculations were terminated when all calculated shifts were less than 0.05 $\sigma$  and  $R$  and  $R_w$  0.086 and 0.106 respectively, with  $w = 1/[\sigma^2(F) + 0.00015F^2]$ . The residual electron density in a final difference map was within -0.93 to 0.84 eÅ<sup>-3</sup>.

Computations were carried out largely with SHELX [14] on a CDC7600 at the University of Manchester Regional Computer Centre via a direct data link. Figures were drawn with PLUTO [15]. Atomic coordinates are given in Table 1. Tables of thermal parameters and observed and calculated structure factors are available from the authors.

#### Results and discussion

Bond lengths and angles are listed in Table 2 and selected torsion angles are in Table 3. A stereoscopic view of the molecule in a direction perpendicular to the

Table 2

Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Fe(1)–C(1)	2.046(11)	C(6)–O(1)	1.225(12)
Fe(1)–C(2)	2.010(10)	C(6)–N(1)	1.334(13)
Fe(1)–C(3)	2.074(11)	C(13)–O(4)	1.225(12)
Fe(1)–C(4)	2.043(10)	C(13)–N(2)	1.339(13)
Fe(1)–C(5)	2.023(9)	N(1)–C(7)	1.485(13)
Fe(1)–C(1')	2.026(9)	N(1)–C(14)	1.474(11)
Fe(1)–C(2')	2.033(10)	N(2)–C(12)	1.464(12)
Fe(1)–C(3')	2.035(11)	N(2)–C(19)	1.494(12)
Fe(1)–C(4')	2.031(10)	C(7)–C(8)	1.521(14)
Fe(1)–C(5')	2.049(10)	C(8)–O(2)	1.395(12)
C(1)–C(2)	1.399(15)	C(9)–C(10)	1.467(16)
C(1)–C(5)	1.426(15)	C(9)–O(2)	1.439(12)
C(2)–C(3)	1.397(17)	C(10)–O(3)	1.430(13)
C(3)–C(4)	1.421(15)	C(11)–C(12)	1.520(14)
C(4)–C(5)	1.425(14)	C(11)–O(3)	1.425(11)
C(5)–C(6)	1.494(14)	C(14)–C(15)	1.506(15)
C(1')–C(2')	1.402(15)	C(15)–O(5)	1.416(14)
C(1')–C(5')	1.464(13)	C(16)–C(17)	1.460(16)
C(2')–C(3')	1.431(14)	C(16)–O(5)	1.428(12)
C(3')–C(4')	1.364(15)	C(17)–O(6)	1.425(10)
C(4')–C(5')	1.431(13)	C(18)–C(19)	1.512(12)
C(5')–C(13)	1.472(14)	C(18)–O(6)	1.406(11)
C(2)–C(1)–C(5)	105.9(11)	C(6)–N(1)–C(14)	116.9(9)
C(1)–C(2)–C(3)	112.2(11)	C(7)–N(1)–C(14)	116.6(8)
C(2)–C(3)–C(4)	105.1(10)	C(13)–N(2)–C(12)	117.5(8)
C(3)–C(4)–C(5)	109.3(10)	C(13)–N(2)–C(19)	123.7(9)
C(1)–C(5)–C(4)	107.5(9)	C(12)–N(2)–C(19)	115.3(8)
C(1)–C(5)–C(6)	134.0(10)	N(1)–C(7)–C(8)	112.4(8)
C(4)–C(5)–C(6)	118.5(10)	C(7)–C(8)–O(2)	109.9(9)
C(2')–C(1')–C(5')	109.1(8)	C(10)–C(9)–O(2)	112.5(8)
C(1')–C(2')–C(3')	107.2(10)	C(9)–C(10)–O(3)	112.6(9)
C(2')–C(3')–C(4')	108.7(10)	C(12)–C(11)–O(3)	110.2(8)
C(3')–C(4')–C(5')	110.9(9)	N(2)–C(12)–C(11)	115.4(8)
C(1')–C(5')–C(4')	104.1(8)	C(8)–O(2)–C(9)	114.5(8)
C(1')–C(5')–C(13)	131.7(8)	C(10)–O(3)–C(11)	112.8(8)
C(4')–C(5')–C(13)	124.2(8)	N(1)–C(14)–C(15)	112.5(8)
C(5)–C(6)–O(1)	117.0(10)	C(14)–C(15)–O(5)	107.5(9)
C(5)–C(6)–N(1)	122.2(10)	C(17)–C(16)–O(5)	108.7(9)
O(1)–C(6)–N(1)	120.8(9)	C(16)–C(17)–O(6)	108.2(9)
C(5')–C(13)–O(4)	116.7(9)	C(19)–C(18)–O(6)	108.9(8)
C(5')–C(13)–N(2)	122.0(10)	N(2)–C(19)–C(18)	113.1(8)
O(4)–C(13)–N(2)	121.2(10)	C(15)–O(5)–C(16)	115.5(9)
C(6)–N(1)–C(7)	125.3(8)	C(17)–O(6)–C(18)	112.1(8)

planes of the cyclopentadienyl rings, giving the crystallographic atom numbering scheme is shown in Fig. 1.

The 18-membered heterocyclic ring shows no obvious symmetry and its conformation is described by the torsion angles listed in Table 3. Seven of these are in the range 163–177°, ten are in the range 69–87° and one is intermediate in value at 126°. The ring is more puckered than the parent 1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane in the solid state. Here the ring is more symmetrical and

Table 3

Selected torsion angles ( $^{\circ}$ ); e.s.d.'s are ca.  $1^{\circ}$ 

N(1)–C(7)–C(8)–O(2)	172.8
C(7)–C(8)–O(2)–C(9)	–80.5
C(8)–O(2)–C(9)–C(10)	165.7
O(2)–C(9)–C(10)–O(3)	–72.3
C(9)–C(10)–O(3)–C(11)	87.5
C(10)–O(3)–C(11)–C(12)	–169.2
O(3)–C(11)–C(12)–N(2)	78.8
C(11)–C(12)–N(2)–C(19)	–126.4
C(12)–N(2)–C(19)–C(18)	80.5
N(2)–C(19)–C(18)–O(6)	77.9
C(19)–C(18)–O(6)–C(17)	173.7
C(18)–O(6)–C(17)–C(16)	–177.3
O(6)–C(17)–C(16)–O(5)	–69.3
C(17)–C(16)–O(5)–C(15)	163.5
C(16)–O(5)–C(15)–C(14)	–167.1
O(5)–C(15)–C(14)–N(1)	68.9
C(15)–C(14)–N(1)–C(7)	–83.2
C(14)–N(1)–C(7)–C(8)	–82.6
C(5)–C(6)–N(1)–C(7)	–12.8
O(1)–C(6)–N(1)–C(14)	1.6
C(5)–C(6)–N(1)–C(14)	179.7
C(5')–C(13)–N(2)–C(19)	11.4
O(4)–C(13)–N(2)–C(12)	–8.0
C(5')–C(13)–N(2)–C(12)	169.2

more open. The C–X–C–C' (X = N or O) moieties have *trans* (antiperiplanar) conformations, torsion angles  $176$ – $179^{\circ}$  and the O–C–C–O and N–C–C–O moieties have *gauche* (synclinal) conformations, torsion angles  $64$ – $73^{\circ}$  [16].

The puckering of the ring in the title compound may be at least partially due to the presence of extra linkage between the two nitrogen atoms, forcing these atoms closer together, the N...N distance being  $5.220(10)$  Å compared with  $5.843(5)$  Å in the parent molecule. The 18-membered ring of the 7,16-diphenyl derivative of the parent molecule is also highly puckered and unsymmetrical [17] and this has been attributed to the steric requirements of the phenyl substituents, but the effects of packing forces may also be important.

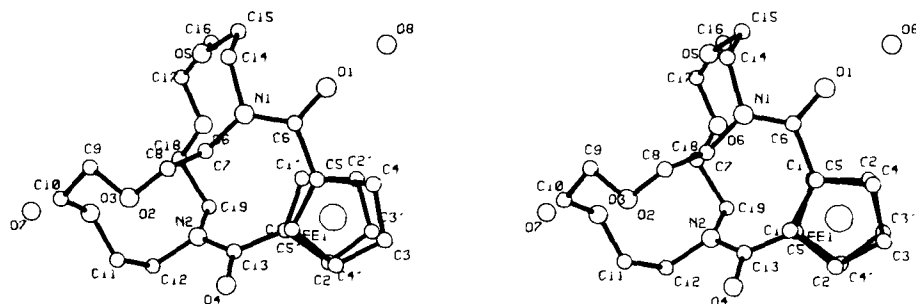


Fig. 1. Stereoscopic view of the title compound perpendicular to the planes of the cyclopentadienyl rings.

Bond lengths in the heterocyclic ring generally agree with expected values (see Table 2). The carbon-carbon bonds fall into two categories; those flanked by two oxygen atoms have lengths 1.467(16) and 1.460(16) Å, and those flanked by a nitrogen and an oxygen atom have lengths in the range 1.506(15) to 1.521(14) Å. This difference in C-C bond lengths may be attributed to the greater rehybridisation effect of oxygen relative to the less electronegative nitrogen. A similar distinction between the two classes of C-C bonds occurs also in the parent molecule [16].

The amide bonds C(6)-N(1) and C(13)-N(2), 1.334(13) and 1.339(13) Å have bond lengths closer to a C-N double bond (1.28 Å) than to a single bond (1.47 Å), due to these bonds being involved in electron delocalisation between the nitrogen lone pair and the carbonyl oxygen atom. The disposition of valencies about each of the amide bonds is near planar with torsion angles close to zero ( $2-13^\circ$ ), or close to  $180^\circ$  (actual values in the range  $166-180^\circ$ ). The sum of valency angles at the nitrogen atoms,  $358.8^\circ$  at N(1) and  $356.5^\circ$  at N(2) do, however, indicate a flattened pyramidal geometry at nitrogen, rather than precise planarity.

The ferrocene moiety has planar cyclopentadienyl rings which are very nearly parallel, interplanar angle  $0.4^\circ$ , with an average separation of 3.286 Å. The Fe-C distances are in the range 2.010 to 2.074, mean 2.037 Å. The cyclopentadienyl bond lengths average 1.416 Å. The two rings are rotated from the eclipsed orientation by ca.  $6.4^\circ$ . These parameters are similar to those found in, inter alia, the low temperature triclinic [18] and orthorhombic [19] forms of ferrocene, 1-acetyl-1'-benzoyl-ferrocene [20], acetyl-ferrocene [21], diacetyl-ferrocene [22] and ferrocene-carboxylic acid [23]. In these compounds however, the cyclopentadienyl ring orientations range from precisely eclipsed [19,22] to a  $14^\circ$  rotation from eclipsed [20].

There are two molecules of water, (07) and (08), for each molecule of the title compound, situated outside the ring system (see Fig. 1). The water hydrogen atoms have not been located; however, on the basis of the observed O...O distances, hydrogen bonds (07)-(03), 2.861(10) Å; (07)...(07) ( $-x, 1-y, 1-z$ ), 2.862(10) Å; (08)...(01), 2.686(10) Å and (07)...(08) ( $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ), 2.820(10) Å occur. These link the macrocycles in the crystal. It is noteworthy that crystals of the title compound could not be obtained in the absence of traces of water.

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