H-atom parameters

\[ w = \frac{1}{\sigma^2(F^2_O) + (0.0570P)^2} \]

where \( P = (F^2_O^2 + 2F^2_C^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} = 0.012 \)

<table>
<thead>
<tr>
<th>Symmetry code</th>
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<th>Ci&lt;sub&gt;1&lt;/sub&gt;-Pt</th>
<th>Ci&lt;sub&gt;3&lt;/sub&gt;-Pt</th>
<th>Ci&lt;sub&gt;1&lt;/sub&gt;-Pt-</th>
<th>Ci&lt;sub&gt;2&lt;/sub&gt;-O1</th>
<th>Ci&lt;sub&gt;2&lt;/sub&gt;-Pt</th>
<th>Ci&lt;sub&gt;2&lt;/sub&gt;-Pt-</th>
<th>Ci&lt;sub&gt;2&lt;/sub&gt;-Pt-</th>
<th>Ci&lt;sub&gt;3&lt;/sub&gt;-Pt-</th>
<th>Ci&lt;sub&gt;1&lt;/sub&gt;-C1</th>
<th>Ci&lt;sub&gt;1&lt;/sub&gt;-C1-</th>
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<th>Ci&lt;sub&gt;4&lt;/sub&gt;-S</th>
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<th>Ci&lt;sub&gt;8&lt;/sub&gt;-S</th>
<th>Ci&lt;sub&gt;8&lt;/sub&gt;-S-</th>
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<tr>
<td>(i) 2 - x, 1/2 + y, 1 - z</td>
<td>1.203 (9)</td>
<td>1.317 (9)</td>
<td>1.521 (10)</td>
<td>1.484 (8)</td>
<td>1.517 (10)</td>
<td>1.534 (8)</td>
<td>1.781 (7)</td>
<td>1.777 (7)</td>
<td>1.450 (6)</td>
<td>2.321 (3)</td>
<td>2.663 (3)</td>
<td>125.6 (7)</td>
<td>123.2 (7)</td>
<td>111.1 (6)</td>
<td>90.48 (8)</td>
<td>91.76 (10)</td>
<td>178.26 (9)</td>
<td>123.2 (7)</td>
<td>125.6 (2)</td>
<td>2.321 (3)</td>
<td>2.663 (3)</td>
<td>125.6 (7)</td>
<td>123.2 (7)</td>
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</tr>
</tbody>
</table>

Table 1. Selected geometric parameters (Å, °)

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged, as is the loan of chemicals by Degussa (Hanau).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1320). Services for accessing these data are described at the back of the journal.

References


Intramolecular C-H···O and intermolecular N-H···O and C-H···O interactions in N-ferrocenoylglycine benzyl ester, an effective dihydrogen phosphate anion sensing agent

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Abstract

The title compound, benzyl N-(ferrocenecarbonyl)glycinate, [Fe(C2H5)(C15H14NO3)], a glycine benzyl ester derivative, is an effective anion sensor for electrochemically sensing the dihydrogen phosphate anion (H2PO4·). Intermolecular N-H···O hydrogen bonds form one-dimensional chains with graph set C(4). [N···O = 2.811 (3) Å]. A two-dimensional network is formed by linking the chains through CmH--O and intermolec-

Comment

The design of new redox-active ligands for application in diverse research areas such as medicinal chemistry and materials science has engrossed scientists in recent years. Ferrocene derivatives, which are efficient redox systems, have been studied extensively in charge-transfer chemistry, hydrogen-bonding and molecular-recognition science, peptide chemistry and non-linear optical materials (Moore et al., 1993; Chesney et al., 1998; Glidewell et al., 1997; Degani & Heller, 1986; Kraatz et al., 1997; Long, 1995). Anion recognition is
of current interest, especially with regard to the design of molecular sensing and switching devices (Beer, 1998; Kingston et al., 1999). An understanding of the interactions present in the crystal structure of a potential anion receptor can provide valuable information on the hydrogen-bonding modes and binding sites in solution studies. The structure of N-ferrocenoylglycine benzyl ester, (I), is reported herein.

![Compound (I)](image)

In the asymmetric unit, molecules of (I) associate through intermolecular N–H⋯O hydrogen bonds [N1⋯O1 2.811(3) Å; symmetry code: (i) x, 1/2 − y, 1/2 + z], forming a one-dimensional chain with graph set C(4) as depicted in Fig. 2 (details in Table 2). The chains are linked through C⋯H⋯O⋯C interaction [C32⋯O3 3.406 (4) Å; symmetry code: (ii) −x, −y, 1−z] about inversion centres with graph set R(8). The N–H⋯O⋯C hydrogen-bonding arrangement with graph set C(4) is present in (II) [N⋯O 2.804 (3) Å], with a C⋯H⋯O interaction [C⋯O 3.309 (4) Å] completing the intermolecular hydrogen bonding; an analogous C⋯H⋯O⋯C intramolecular interaction [C⋯O 3.364 (4) Å] is also observed. The hydrogen-bonding patterns in the crystal structures of a diverse range of ferrocene alcohol derivatives have been reported (Ferguson et al., 1993; Gallagher et al., 1994; Glidewell et al., 1997). For example, benzoylefroccenyl diphenylmethanol forms a

The dihedral angle between the C5 planes is 2.8 (2)° with the rings deviating from the fully eclipsed conformation by 5.1 (3)° [range 4.6 (2)−5.5 (3)°]. The Fe to cyclopentadienyl ring centroid distance is 1.6427 (14) Å for the substituted ring and 1.6461 (16) Å for the unsubstituted ring (Spek, 1998), which are comparable with values of 1.6449 (4) and 1.6464 (4) Å in the related methyl ester derivative, (II) (Gallagher et al., 1999). The range of C⋯C distances in (I) is 1.400 (4)−1.428 (4) Å [mean 1.412 (4) Å] and 1.398 (5)−1.407 (5) Å [mean 1.401 (5) Å] for the substituted and unsubstituted rings, respectively. The Csp3 atom, C1, is displaced by 0.030 (5) Å from the substituted C5 ring plane towards the Fe atom due to the intramolecular interaction C21−H21⋯O2, and the amide C1/O1/N1/C2 plane is at an angle of 16.6 (2)° to the C11−C15 plane [these values are 0.032 (5) Å and 16.67 (17)° in (II), respectively]. The Fe1−C11−C1 angle of 124.74 (17)° is similar to the value of 124.87 (17)° in (II).
dimer with graph set $R_2^1(16)$ through C--H···O hydrogen bonds (Glidewell et al., 1997). We have recently described cyclic (pyrrole)N--H···π(pyrrole) hydrogen bonding involving four pyrrole groups in bis(2-pyrrolyl)methylferrocene, an organometallic porphyrin precursor (Gallagher & Moriarty, 1999).

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for molecules containing the $N$-ferrocenoyl moiety indicates that many of these structures contain a macrocyclic component (Beer, 1998). Several heterobimetallic macrocyclic receptors (Kingston et al., 1999) exhibit electrochemical shifts of a similar magnitude to that observed in (I) with $H_2PO_4^-$. However mono- and disubstituted ferrocene structures contain a macrocyclic component (Beer, 1999). We have recently described cyclic (pyrrole)N...Tr(pyrrole) hydrogen bonds (Glidewell et al., 1999) for molecules containing bis(2-pyrrolyl)methylferrocene, an organometallic porphyrin precursor (Gallagher & Moriarty, 1999).

**Experimental**

The title compound was synthesized according to the literature method of Gallagher et al. (1999). Dark-yellow crystals were recrystallized from ethyl acetate/petroleum ether (b.p. 313–333 K) in 80% yield.

**Crystal data**

[Fe(C,H3)2(C16H14NO3)]

$M_r = 377.21$

Monoclinic $P2_1/c$

$a = 7.9167 (7)$ Å

$b = 22.1936 (16)$ Å

$c = 9.9382 (11)$ Å

$β = 96.612 (11)^o$

$V = 1734.5 (3)$ Å$^3$

$Z = 4$

$D_r = 1.444$ Mg m$^{-3}$

$D_m$ not measured

**Data collection**

Enraf–Nonius CAD-4 diffractometer

$ω$ scans

Absorption correction:

ψ scan (3 ψ scans; North et al., 1968)

$T_{min} = 0.732$, $T_{max} = 0.818$

3405 measured reflections

3222 independent reflections

**Refinement**

Refinement on $F^2$

$R[F^2 > 2σ(F^2)] = 0.043$

$wR(F^2) = 0.085$

$S = 1.020$

3222 reflections

227 parameters

H-atom parameters constrained

$w = 1/[σ^2(F^2) + (0.0331P)^2 + 0.3662P]$

where $P = (F^2 + 2F'^2)/3$

**Table 1. Selected geometric parameters (Å, °)**

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<thead>
<tr>
<th></th>
<th>D--H···A</th>
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<tbody>
<tr>
<td>N1--H1···O1'</td>
<td>0.86</td>
<td>2.01</td>
<td>2.811 (3)</td>
<td>154</td>
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<tr>
<td>C32--H32···O3a</td>
<td>0.93</td>
<td>2.54</td>
<td>3.406 (4)</td>
<td>156</td>
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<tr>
<td>C21--H21···O3</td>
<td>0.93</td>
<td>2.63</td>
<td>3.540 (3)</td>
<td>165</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) $x, ½ - y, ½ + z$; (ii) $-x, -y, 1 - z$.

**Table 2. Hydrogen-bonding geometry (Å, °)**

<table>
<thead>
<tr>
<th></th>
<th>D--H···A</th>
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</table>

**References**


Nitrilotriacetic acid (NTA) is found as a multidentate ligand in many metal–chelate compounds (Skrzypczak-Jankun & Smith, 1994; Martell, 1975). A magnesium-chelated NTA complex has been proposed recently as a guest species within a layered double hydroxide (Kaneyoshi & Jones, 1999). The crystal structure of the title compound, (I), contains Mg atoms chelated by NTA molecules via three Mg—O bonds [2.042 (2)—2.096 (2) Å] and one Mg—N bond [Mgl—N1 2.232 (2) Å]. In addition, each Mg atom is bound to one O atom of a neighbouring NTA molecule [Mgl—O5' 2.029 (2) Å; symmetry code: (i) 2 - x, y + 1/2, z] and one O atom of a water molecule [Mgl—O7 2.066 (2) Å], resulting in a distorted octahedral coordination geometry. The Na atoms are also octahedrally coordinated by four O atoms of different NTA molecules [2.385 (2)—2.453 (2) Å] and two O atoms of water molecules [Na1—O8 2.402 (2) and Na1—O9 2.331 (2) Å].

The three carboxylate groups of each NTA molecule adopt different bonding patterns. The first (C2, O1 and O2) binds to the chelated Mg atom and one Na atom via O2, and is involved in interlayer hydrogen bonding through O1 [O1 ii—..08 2.762(3) Å and O1 ii—H8A—08 167(3)°; symmetry code: (ii) 2 - x, y + 1/2, z]. The second (C4, O3 and O4) binds to one Mg atom and one Na atom via O3 and O4, respectively. In the third carboxylate group (C6, O5 and O6), O5 and O6 each bind to both an Mg atom and an Na atom, acting as bridges between adjacent MgNa(C6H6NO6)(H2O)3 units.

The interactions between the metal atoms and the NTA ligands, together with hydrogen-bonding interactions, give rise to infinite MgNa(C6H6NO6)(H2O)3 layers.