Compounds (I) and (II) both crystallized in the monoclinic system, space groups $P2_1/n$ and $P2_1/a$, respectively, from the systematic absences. $H$ atoms were treated as riding atoms with $C-H \approx 0.93 \AA$.

For both compounds, data collection: CAD-4-PC (Enraf-Nonius, 1992); cell refinement: SET4 and CELDIM in CAD-4-PC; data reduction: DATR2D in NRCVAX (Gabe et al., 1989); program(s) used to solve structures: NRCVAX via Patterson heavy-atom method; program(s) used to refine structures: NRCVAX and SHELXL97 (Sheldrick, 1997); molecular graphics: NRCVAX, ORTEPII (Johnson, 1976); PLATON (Spek, 1997a) and PLUTON (Spek, 1997b); software used to prepare material for publication: NRCVAX, SHELXL97 and WordPerfect macro PRPCIF97 (Ferguson, 1997).

JFG thanks the Research and Postgraduate Committee of Dublin City University, the Royal Irish Academy and Forbairt for generous funding of a research visit to the University of Guelph (June–August, 1997). SZA thanks the Committee of Vice-Chancellors and Principals (UK) and the University of St Andrews for financial support.

References

1776
[Fe(C_{12}H_{2}O)(C_{18}H_{15}O)]

2.891 (2) Å; the ferrocenyl unit adopts an eclipsed conformation and the molecules are linked into centrosymmetric dimers by C--H···O hydrogen bonds with C···O 3.357 (3) Å, to generate a cyclic $R_4^2(16)$ motif.

Comment
Substituted diphenylmethanols $R$CPh$_2$OH exhibit a very wide range of hydrogen-bonding patterns in the solid state (Ferguson et al., 1995). When $R$ is ferrocenyl [(C$_5$H$_9$)$_2$Fe(C$_5$H$_4$)], the resulting ferrocenyl-diphenylmethanol, [(C$_5$H$_9$)$_2$Fe(C$_5$H$_4$)]CPh$_2$OH, crystallizes as cyclic centrosymmetric dimers (Ferguson et al., 1993a) characterized by an (OH)$_2$ motif with graph set $R_2^2(14)$ (Bernstein et al., 1995), while the analogous ferrocene-1,1'-diylbis(diphenylmethanol), Fe[(C$_5$H$_4$)CPh$_2$OH]$_2$, (in which both cyclopentadienyl rings carry a strong hydrogen-bond donor substituent) forms dimers based on an $R_4^2(8)$ motif in which the hydroxyl H atoms appear to be disordered (Ferguson et al., 1993a), but are in fact mobile between pairs of non-equivalent sites (Aliev et al., 1995). Continuing our study of the hydrogen-bonding patterns in ferrocenyl alcohols (Glidewell et al., 1996), we have investigated the structure of (1'-benzoylferrocenyl)diphenylmethanol, [(PhCOC$_5$H$_4$)Fe(C$_5$H$_4$)]CPh$_2$OH, (I), in which the cyclopentadienyl ring not carrying the CPh$_2$OH substituent has a strong hydrogen-bond accepting benzoyl group. Compound (I) thus contains an excess of hard (Braga et al., 1995) hydrogen-bond acceptors over hard donors, and consequently the occurrence of C--H···O hydrogen bonds is to be expected.

In compound (I) (Fig. 1), there are both intra- and intermolecular hydrogen bonds (Table 2). There is an intramolecular O—H···O hydrogen bond in which the hydroxyl and carbonyl O atoms act as a hydrogen-bond donor and acceptor, respectively, to give a motif whose graph set is $S(8)$; this resembles the intramolecular O—H···O hydrogen bond in Fe[(C$_5$H$_4$)CPh$_2$OH]$_2$ (Ferguson et al., 1993a). In addition, there is an intramolecular C—H···O hydrogen bond; atom C53 in the benzoyl group (Fig. 1) at $(x,y,z)$ acts as hydrogen-bond donor to the hydroxyl atom O1 at $(-x,2-y,-z)$, while C53 at $(-x,2-y,-z)$ in turn acts as a donor towards O1 at $(x,y,z)$. In this way, a cyclic dimer is generated, with graph set $R_4^2(16)$ and lying about the inversion centre at $(0,1,0)$ (Fig. 1). There are no short intermolecular contacts involving the carbonyl O atom and it is noteworthy that it is the hydroxyl O atom which acts as the acceptor in the intermolecular C—H···O hydrogen bond, although the electrostatic nature of such interactions (Taylor & Kennard, 1982) means that carbonyl O atoms generally behave as more powerful hydrogen-bond acceptors than ether or alcohol O atoms (Desiraju, 1991, 1996).

Within the molecules of (I), the distances of the Fe atom from the centroid of the rings defined by C1n and C2n ($n = 1–5$) are 1.6437 (4) and 1.6405 (4) Å, respectively, and the angle subtended at the iron by the ring centroids is 176.65 (2)°. There are three conformational variables of significance: the relative twist of the cyclopentadienyl rings and the conformation about the two independent exocyclic C—C bonds. A convenient measure of the relative twist of the rings is provided by the torsion angle C11—Cg1—Cg2—C21, where Cg1 and Cg2 represent the centroids of the two cyclopentadienyl rings; since the rings do not have local C$_5$ symmetry, the mean value of the torsion angles C1n—Cg1—Cg2—C2n ($n = 1–5$) provides the appropriate measure; for perfect eclipsing of the rings, this value is $(72 \times n)°$, where $n = 0$ or integer and $n = 0$ signifies that bonds C11—C1 and C21—C2 are also eclipsed. In compound (I), the mean twist angle is 70.4 (1)°, indicative of nearly eclipsed rings with the exocyclic C—C bonds offset by one fifth of a revolution. This is the conformation in Fe[(C$_5$H$_4$)CPh$_2$OH]$_2$ (Ferguson et al.,

![Fig. 1. A view of the dimeric aggregate in (I) showing the atom-numbering scheme, the O—H···O and C—H···O hydrogen bonds and the centrosymmetric $R_4^2(16)$ ring. Displacement ellipsoids are drawn at the 30% probability level.](image-url)
Refinement

Refinement on $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.097$

$S = 0.970$

6052 reflections

302 parameters

H atoms; see below

$w = 1/\sigma^2(F^2) + (0.064P)^2$

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

Table 1. Selected geometric parameters (Å, °)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1---C1</td>
<td>1.516(3)</td>
<td>111.30(9)</td>
</tr>
<tr>
<td>C2---C2</td>
<td>1.377(3)</td>
<td>112.83(9)</td>
</tr>
<tr>
<td>C3---C3</td>
<td>1.513(3)</td>
<td>110.35(9)</td>
</tr>
<tr>
<td>C4---C4</td>
<td>1.536(3)</td>
<td>110.50(9)</td>
</tr>
<tr>
<td>C5---C5</td>
<td>1.491(3)</td>
<td>108.74(9)</td>
</tr>
<tr>
<td>C6---C6</td>
<td>1.526(3)</td>
<td>110.75(9)</td>
</tr>
<tr>
<td>C7---C7</td>
<td>1.510(3)</td>
<td>110.80(9)</td>
</tr>
<tr>
<td>C8---C8</td>
<td>1.495(3)</td>
<td>108.90(9)</td>
</tr>
<tr>
<td>C9---C9</td>
<td>1.477(3)</td>
<td>110.50(9)</td>
</tr>
<tr>
<td>C10---C10</td>
<td>1.425(3)</td>
<td>108.74(9)</td>
</tr>
<tr>
<td>C11---C11</td>
<td>1.402(3)</td>
<td>107.85(9)</td>
</tr>
<tr>
<td>C12---C12</td>
<td>1.402(3)</td>
<td>107.85(9)</td>
</tr>
<tr>
<td>C13---C13</td>
<td>1.414(4)</td>
<td>109.90(9)</td>
</tr>
<tr>
<td>C14---C14</td>
<td>1.401(4)</td>
<td>109.90(9)</td>
</tr>
<tr>
<td>C15---C15</td>
<td>1.392(4)</td>
<td>109.90(9)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>H···A</th>
<th>D---H</th>
<th>H···A</th>
<th>D···A</th>
<th>D---H</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1---H1---O2</td>
<td>0.76(2)</td>
<td>2.19(3)</td>
<td>2.89(2)</td>
<td>154(3)</td>
</tr>
<tr>
<td>O1---H1---O2</td>
<td>0.93(2)</td>
<td>2.49(3)</td>
<td>3.35(3)</td>
<td>156</td>
</tr>
</tbody>
</table>

Symmetry code: (i) = -x, 2-y, -z.

Compound (I) crystallized in the monoclinic system; space group P21/n from the systematic absences. H atoms attached to C atoms were allowed for as riding atoms with C—H 0.93 Å; the hydroxy H atom was located from a difference map and refined isotropically.

Data collection: CAD-4-PC (Enraf–Nonius, 1992). Cell refinement: SET4 and CELDIN in CAD-4-PC. Data reduction: DATRVD2 in NRCVAX (Gabe et al., 1989). Program(s) used to solve structure: SHELX97 (Sheldrick, 1997a). Program(s) used to refine structure: NRCVAX96 and SHELXL97 (Sheldrick, 1997b). Molecular graphics: NRCVAX96, ORTEPII (Johnson, 1976), PLATON (Spek, 1997a) and PLUTON (Spek, 1997b). Software used to prepare material for publication: NRCVA96, SHELXL97 and WordPerfect macro PRPCIF97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SKI147). Services for accessing these data are described at the back of the journal.
References


(1,4,7,11,13-Pentaazacyclohexadecane-\(\kappa^5\)N)-perchlorato-\(\kappa^O\)nickel(II) Perchlorate

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Abstract

The crystal structure of the title compound, [Ni(ClO\(_4\))\((\text{C}_{11}\text{H}_{27}\text{N}_{5})\]ClO\(_4\)], shows that the Ni\(^{II}\) ion is six-coordinate involving the pentadentate macrocycle and one perchlorate O atom. There are two independent molecules in the asymmetric unit. The conformation of the ligand is in the most stable form, with the six-membered ring in a chair form and all four five-membered rings in gauche forms.

Comment

Polyaza macrocyclic ligands have attracted interest from coordination chemists, but most attention has been paid to tetradentate macrocycles, less information being available for larger ring systems. The Richman & Atkins (1974) procedure allows the simple and general synthesis of larger ring systems. Reported studies have been concerned with the thermodynamics and kinetics of the metal complexes of pentaaza macrocycles in solution (Kodama & Kimura, 1978a,b; Hay, Bembi, Moodie & Norman, 1982; Hay, Bembi, McLaren & Moodie, 1984). Little work has been carried out on the crystal structures of metal complexes of pentaaza macrocycles (Bombieri et al., 1982; Eigenbrot et al., 1988; Tahir et al., 1993). The present paper reports the crystal structure of the title compound, [Ni(ClO\(_4\))(\text{C}_{11}\text{N}_{5}\text{H}_{27})]ClO\(_4\), (I).

The structure of (I) consists of two crystallographically independent [Ni(ClO\(_4\))(\text{C}_{11}\text{N}_{5}\text{H}_{27})]\(^{+}\) complex cations (denoted as molecules A and B) and two perchlorate anions. Both molecules have nearly the same conformation, and bond lengths and angles have normal values. The complex cation is six-coordinate, with five N atoms of the pentaaza macrocycle and a perchlorate O atom around the Ni\(^{II}\) ion. The macroyclic ligand is coordinated with a 5,6,5 arrangement of the chelate rings in the equational plane containing four N atoms. The N3 and N4 atoms have opposite chirality giving the meso-syn diastereoisomer (Bombieri et al., 1982). The configurations of the four chiral amine N centers are 1RS, 4RS, 10SR and 13SR. The conformation of the ligand is the most stable form, with the six-membered ring in a chair form and all four five-membered rings in gauche forms. The overall geometry is similar to that of an analogous cobalt(III) complex (Bombieri et al., 1982). The crystal structure is stabilized by a three-dimensional network of N–H···O hydrogen bonds, as given in Table 2. The second perchlorate anion is free in the lattice and participates in the hydrogen bonding.

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