Coverage of the unique set is over 97% complete to at least 26° in θ. Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. Anisotropic temperature factors were used for all non-H atoms; H atoms were given isotropic temperature factors equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: SMART (Siemens, 1994). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXS96 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL96 (Sheldrick, 1996b). Molecular graphics: SHELXTL/PC (Sheldrick, 1994). Software used to prepare material for publication: SHELXTL/PC.

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3-Ferrocenyl-6-nitro-2-phenylquinoxaline: Cyclic Centrosymmetric Dimers Depending on both C—H···O Hydrogen Bonds and π–π Stacking Interactions†

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Abstract

Molecules of 3-ferrocenyl-6-nitro-2-phenylquinoxaline, $[\text{Fe}(C_5H_5)(C_{19}H_{12}N_3O_2)]$, are linked by C—H···O hydrogen bonds into centrosymmetric $R_2^2(22)$ dimers, reinforced by π–π stacking interactions. Two independent molecules form two such independent dimers which pack together in a pseudo-CsCl structure.

Comment

The reaction of 1-ferrocenyl-2-phenylethanedione with substituted 1,2-diaminobenzenes yields the corresponding substituted ferrocenyl(phenyl)quinoxalines as pairs of regioisomers, which are usually inseparable by chromatography (Zanello et al., 1998). Thus, with 1,2-diamino-4-nitrobenzene, a mixture of two quinoxalines is formed with an isomer ratio of ca 3:1; the identity of the more abundant isomer could not be deduced from the NMR data. However, careful chromatography of this mixture afforded a crystalline material which appeared from NMR and TLC observations to consist of a single isomer, and the structure of this material is reported here. It proved, in fact, to be a 5:1 mixture of the two regioisomers, with 3-ferrocenyl-6-nitro-2-phenylquinoxaline, (I), as the major component and 2-ferrocenyl-6-nitro-3-phenylquinoxaline, (II), as the minor component.

(I) (Fc = ferrocenyl)   (II)

The mixture crystallized in space group $P\bar{1}$ with two molecules in the asymmetric unit; because of

the fused-ring structure of the quinoxaline on the one hand and $Z' = 2$ on the other, no attempt has been made to harmonize the atom-labelling scheme used here with standard chemical numbering conventions. Both molecular sites in the asymmetric unit proved to contain a mixture of the two isomers with ratios derived from the refined site-occupation factors of 0.813 (3):0.187 (3) for molecule 1 (containing Fe1) and 0.860 (3):0.140 (3) for molecule 2. At each site, the locations of the ferrocenyl and phenyl fragments were identical for the major and minor isomers, but the orientations of the quinoxaline fragments differed for the two isomers (Fig. 1). The refinement of isomer (II) was subject to constraints (see Experimental) and all discussion of molecular geometry is therefore confined to isomer (I).

Within the fully eclipsed ferrocene fragments, the mean C—C bond distances for the substituted and unsubstituted rings are 1.416 (13) and 1.392 (9) Å, re-

spectively. In molecule 1, the Fe1—$Cg1$ and Fe1—$Cg2$ distances are 1.637 (2) and 1.642 (2) Å, respectively, with an angle $Cg1$—Fe1—$Cg2$ of 176.1 (1)°, while in molecule 2, the corresponding values of Fe2—$Cg3$, Fe2—$Cg4$ and $Cg3$—Fe2—$Cg4$ are 1.641 (1), 1.649 (1) Å and 176.2 (1)° ($Cg1$–$Cg4$ represent the centroids of the cyclopentadienyl rings C2n, C3n, C6n and C7n, respectively, for $n = 1$–5). For the unsubstituted rings C3n and C7n, the displacement parameters indicate significant torsional motion about the local fivefold axes. The quinoxaline fragments show marked bond fixation of the naphthalene type (Table 1), as observed previously both in other ferrocenylquinoxalines (Ferguson et al., 1995; Glidewell et al., 1996) and in hexachloroquinoxaline (Vermeulen & Huiszoon, 1979). The internal angles at nitrogen (Table 2) are all significantly less than 120°, as typically found in simple pyrazines and quinoxalines.

The overall molecular conformation is very similar to that found in 2-ferrocenyl-3-phenylquinoxaline (Glidewell et al., 1996). In each of the two independent molecules, the quinoxaline fragment is almost coplanar with the substituted cyclopentadienyl ring, with interplanar angles of 2.0 (2) and 3.4 (3)° in molecules 1 and 2, respectively; similarly, the nitro groups are almost coplanar with the quinoxaline rings, with interplanar angles of 2.5 (3) and 8.5 (4)°. In contrast, the phenyl rings make interplanar angles with the quinoxaline rings of 88.2 (1) and 87.8 (1)°, respectively, in the two molecules.

The molecules of (I) are linked into cyclic centrosymmetric dimers by a combination of C—H···O hydrogen bonds and π–π stacking interactions (Table 2 and Fig. 2). Atom C31 in the unsubstituted cyclopentadienyl ring of molecule 1 at (x, y, z) acts as donor to O1 in molecule 1 at $(1-x, 1-y, 2-z)$, so generating an $R_2^2(22)$ motif (Bernstein et al., 1995) for the dimer centred at $(\frac{1}{2},\frac{1}{2},1)$. The corresponding C71 atom in molecule 2 at (x, y, z) acts as donor towards O3 in molecule 2 at $(-x, 2-y, 1-z)$, so generating a second $R_2^2(22)$ motif for the dimer centred at $(0,1,\frac{1}{2})$. The two types of cyclic dimer thus pack to form a pseudo-CsCl type structure (Fig. 3). Entirely similar C—H···O hydrogen bonds are formed by isomer (II), with atoms O1A and O3A (whose positions are very close to those of O1 and O3, respectively) as acceptors (Table 2). The C—H···O hydrogen bonds are all nearly linear (Table 2 and Fig. 2); in each case, the H···O and C···O distances and the C—H···O angle indicate that these are fairly strong examples for their types. In addition, the two overlapping quinoxaline units in each dimer exhibit π–π stacking interactions, with interplanar separations of 3.51 and 3.52 Å in the dimers formed by molecules 1 and 2, respectively. The phenyl groups appear to play no role in the dimer formation.

It is of interest to compare the structure of (I) with those of closely related ferrocene derivatives each containing one of the two supramolecular synthons (Desiraju, 1995) evident in (I). Thus, nei-

Fig. 1. Views of the two independent molecules of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Also shown, in each case, are the positions of the minor isomer, (II).
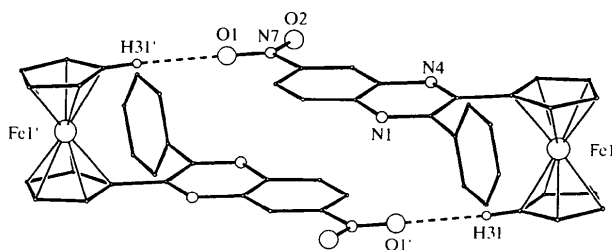
Fig. 2. View of the dimer formed by molecule 1 of isomer (I), showing the C—H···O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.
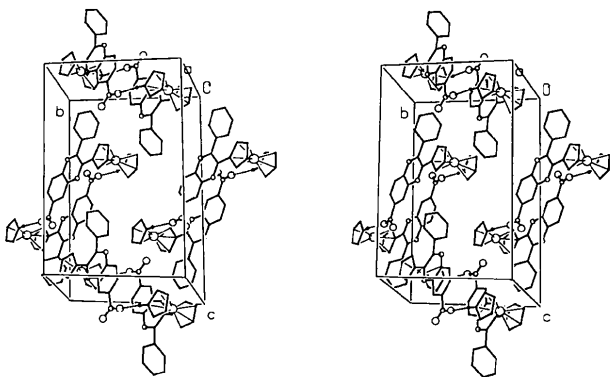

Fig. 3. Stereoview of part of the crystal structure of (I) showing the two independent dimers forming a pseudo-CsCl structure.

ther 2-ferrocenylquinoxaline (Ferguson et al., 1995) nor 2-ferrocenyl-3-phenylquinoxaline (Glidewell et al., 1996) exhibits any π–π stacking interactions, while 4-nitrophenylferrocene (Gallagher et al., 1997) exhibits no C—H···O hydrogen bonding. However, when both of these supramolecular synthons are present, as in (I), supramolecular dimerization of the ferrocenylnitroquinoxaline occurs. The effective co-operation of these two synthons in (I) is almost certainly associated with the fact that the typical interplane spacing in π–π-stacked aromatic systems is very similar to the inter-ring separation in ferrocenes (Fig. 2).

Experimental

The title compound was prepared and purified according to Zanello et al. (1998). Crystals suitable for single-crystal X-ray diffraction were grown from ethyl acetate solution.

Crystal data

[Fe(C_5H_5)($C_{19}H_{12}N_3O_2$)]
$M_r = 435.26$
Triclinic
$P\bar{1}$
$a = 8.3220\,(7)$ Å
$b = 12.5682\,(11)$ Å
$c = 18.6853\,(18)$ Å
$\alpha = 94.663\,(8)°$
$\beta = 96.980\,(7)°$
$\gamma = 95.479\,(6)°$
$V = 1922.4\,(3)$ Å^3
$Z = 4$
$D_x = 1.504$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.40$–$17.76°$
$\mu = 0.812$ mm^{-1}
$T = 294\,(1)$ K
Block
$0.42 \times 0.41 \times 0.31$ mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
  Gaussian (*ABSO* in *NRCVAX*; Gabe et al., 1989)
  $T_{min} = 0.716$, $T_{max} = 0.804$
7087 measured reflections
7076 independent reflections

5046 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 25.36°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = -22 \rightarrow 22$
3 standard reflections
  frequency: 240 min
  intensity variation: 1.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.111$
$S = 0.951$
7076 reflections
575 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.7344P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.225$ e Å^{-3}
$\Delta\rho_{min} = -0.303$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C2	1.308 (4)	N41—C42	1.312 (4)
N1—C10	1.362 (5)	N41—C50	1.350 (4)
C3—N4	1.321 (4)	C43—N44	1.319 (4)
N4—C5	1.379 (5)	N44—C45	1.382 (4)
C7—N7	1.493 (4)	C47—N47	1.486 (3)
N7—O2	1.197 (3)	N47—O4	1.198 (3)
N7—O1	1.197 (3)	N47—O3	1.201 (3)
C2—C11	1.479 (4)	C42—C51	1.471 (4)
C3—C21	1.483 (4)	C43—C61	1.475 (4)
C2—N1—C10	117.7 (3)	C42—N41—C50	118.0 (3)
C3—N4—C5	116.8 (3)	C43—N44—C45	117.4 (3)
O2—N7—O1	126.8 (4)	O4—N47—O3	126.0 (3)
O2—N7—C7	116.5 (3)	O4—N47—C47	116.9 (3)
O1—N7—C7	116.8 (3)	O3—N47—C47	117.1 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C31—H31···O1^i	0.93	2.46	3.391 (6)	176
C71—H71···O3^{ii}	0.93	2.45	3.368 (7)	169
C31—H31···O1A^i	0.93	2.32	3.233 (18)	169
C71—H71···O3A^{ii}	0.93	2.21	3.11 (3)	166

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

The isomer mixture, (I) and (II), crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. The structure was solved readily via the heavy-atom method, but when all the atoms were included, there were

still six significant peaks (0.7–1.0 e Å^{-3}) in a difference map, three each in the neighbourhood of C8 and C48 of the two independent molecules. Although considerable care *via* chromatography had been taken to try to ensure that the sample was a single isomer, it was soon realized that these additional peaks were consistent with a small amount of 2-ferrocenyl-6-nitro-3-phenylquinoxaline being present in addition to the major component, 3-ferrocenyl-6-nitro-2-phenylquinoxaline. The positions of these minor occupancy nitro groups also showed that the quinoxaline framework of the minor isomers did not overlap exactly the sites of the major isomer. Fortunately, we had previously determined the structure of 2-ferrocenyl-3-phenylquinoxaline (Glidewell *et al.*, 1996) and it was a relatively straightforward exercise to take the quinoxaline coordinates from that structure and use these as a template with the *FRAG* command available with *SHELXL*97 (Sheldrick, 1997) and appropriate *DFIX* restraints. Initially, the major and minor quinoxaline components were constrained using the *FRAG* command, but in the final rounds of refinement, these constraints were removed from the two major quinoxaline components. Refinement then proceeded smoothly with the atoms of each minor quinoxaline component allowed an overall isotropic displacement parameter [final values 0.055 (3) and 0.065 (3) Å^2]; the minor nitro-N atoms were assigned a U_{iso} value of 0.080 Å^2 and the minor nitro-O atoms were assigned the value 0.010 Å^2. The final occupancies of the two major/minor components refined to 0.813 (3)/0.187 (3) and 0.860 (3)/0.140 (3). All H atoms were treated as riding atoms (C—H 0.93 Å).

Data collection: *CAD-4-PC* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC*. Data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX96 via* Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX96* and *SHELXL97*. Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PREP8* (Ferguson, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1223). Services for accessing these data are described at the back of the journal.

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Polymeric Chloro(triphenyl trithiophosphite)copper(I)

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Abstract

The title compound, *catena*-poly[copper(I)-μ-chloro-μ-[tris(phenylthio)phosphine-*P:S*]], [CuCl(C₁₈H₁₅PS₃)]$_n$, is polymeric. Only one of the S atoms acts as a donor to copper. Tetrahedrally coordinated Cu^I centres form spiro junctions between five-membered rings (–Cu—Cl—Cu—S—P–), thus forming a helical chain polymer in which the monomeric units are related by a 3_1 screw axis. Bond lengths at copper are Cu—P 2.2434 (16), Cu—Cl 2.3235 (16), Cu—Cl' 2.3351 (15) and Cu—S3' 2.3442 (15) Å.

Comment

Thiophosphites are versatile ligands in view of their diverse potential coordination sites. However, the corresponding coordination chemistry has not been in-

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