Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.050$
$S = 1.010$
2854 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0260P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.371$ e Å^{-3}
$\Delta\rho_{\min} = -0.328$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.00054 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.003 (13)

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

Mo—S1	2.1766 (9)	Ni—N1	2.122 (3)
Mo—S2	2.1791 (10)	Ni—N5	2.123 (3)
Mo—S3	2.1849 (9)	Ni—N3	2.133 (3)
Mo—S4	2.1865 (11)	Ni—N6	2.133 (3)
Ni—N2	2.099 (3)	Ni—N4	2.135 (2)
S1—Mo—S2	109.67 (5)	N5—Ni—N3	94.64 (12)
S1—Mo—S3	110.29 (4)	N2—Ni—N6	93.57 (11)
S2—Mo—S3	109.09 (4)	N1—Ni—N6	91.89 (12)
S1—Mo—S4	109.96 (6)	N5—Ni—N6	82.61 (12)
S2—Mo—S4	107.25 (4)	N3—Ni—N6	91.21 (12)
S3—Mo—S4	110.52 (4)	N2—Ni—N4	93.43 (11)
N2—Ni—N1	81.71 (13)	N1—Ni—N4	96.24 (11)
N2—Ni—N5	173.21 (13)	N5—Ni—N4	91.09 (12)
N1—Ni—N5	92.77 (13)	N3—Ni—N4	81.47 (11)
N2—Ni—N3	91.04 (13)	N6—Ni—N4	169.96 (13)
N1—Ni—N3	172.28 (13)		

All N, S, C, Mo and Ni atoms were refined with anisotropic displacement parameters, except for C1′ and C2′, which are split positions of C1 and C2 and were therefore refined isotropically. The H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters [$U_{\rm iso}$(N—H/C—H) = $1.2U_{\rm eq}$($C_{\rm methylene}$/$C_{\rm amine}$)] using a riding model with the parameters C—H = 0.97 and N—H = 0.90 Å. The absolute structure was determined and is in accordance with the selected setting [Flack *x* parameter = −0.003 (13)].

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1258). Services for accessing these data are described at the back of the journal.

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1,1′-Bis(3-phenylquinoxalin-2-yl)ferrocene dichloromethane solvate

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Abstract

In 1,1′-bis(3-phenylquinoxalin-2-yl)ferrocene dichloromethane solvate, $[\mathrm{Fe(C_{19}H_{13}N_2)_2}]\cdot0.9\mathrm{CH_2Cl_2}$, the two cyclopentadienyl rings are offset by only 21° from being completely eclipsed, so that the near parallel quinoxalinyl groups exhibit considerable overlap, with an interplanar spacing almost ideal for intramolecular π–π stacking interactions. The molecules form columns by means of intermolecular π–π stacking interactions.

Comment

The reaction of 1-ferrocenyl-2-phenylethanedione, FcCOCOPh [Fc is $(\mathrm{C_5H_5})\mathrm{Fe}(\mathrm{C_5H_4})$] with 1,2-diaminobenzene yields ferrocenyl(phenyl)quinoxaline (Zanello *et al.*, 1998). In a similar way, ferrocene-1,1′-diylbis(2-phenylethanedione), $\mathrm{Fe(C_5H_4COCOPh)_2}$, reacts with 1,2-diaminobenzene to yield 1,1′-bis(3-phenylquinoxalin-2-yl)ferrocene, $\mathrm{Fe[C_5H_4(C_8H_4N_2)C_6H_5]_2}$. This compound crystallized from diethyl ether/dichloromethane as a partial 0.9-dichloromethane solvate, (I), in which the solvent molecule is hydrogen bonded to one of the quinoxaline fragments by means of a C—H···N hydrogen bond (Fig. 1 and Table 2).

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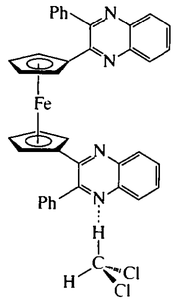

(I)

Within the molecules of compound (I), the Fe—*Cg*1 and Fe—*Cg*2 distances are 1.656 (1) and 1.655 (1) Å, respectively, and the *Cg*1—Fe—*Cg*2 angle is 177.8 (1)° (*Cg*1 and *Cg*2 represent the centroids of the cyclopentadienyl rings C1*n* and C2*n*, respectively, for *n* = 1–5). The mean value of the C—C bond distances in these rings is typical of those observed in other monosubstituted ferrocenylquinoxalines (Ferguson *et al.*, 1995; Glidewell *et al.*, 1996; Ahmed *et al.*, 1998). The quinoxalinyl fragments in (I) both exhibit the bond fixation typical of the heteroaromatic system (Vermeulen & Huiszoon, 1979; Ferguson *et al.*, 1995; Glidewell *et al.*, 1996; Ahmed *et al.*, 1998).

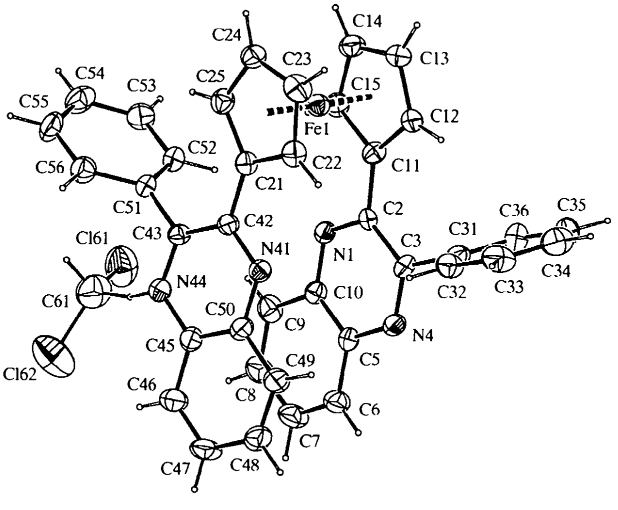

Fig. 1. A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The conformation of (I) and the molecular packing are intimately connected. The independent quinoxalinyl groups are both nearly coplanar with the neighbouring cyclopentadienyl ring, with interplanar angles between the quinoxalinyl and cyclopentadienyl rings of 5.2 (3) and 7.8 (3)° for the fragments containing C11 and C21, respectively, while the dihedral angle between the two quinoxalinyl planes is 5.4 (2)°. Moreover, the mean value of the C1*n*—*Cg*1—*Cg*2—C2*n* torsion angles (*n* = 1–5) is −20.9 (9)°, where a value of zero would indicate perfect eclipsing of both the cyclopentadienyl rings and the exocyclic C—C bonds; consequently, the two independent quinoxalinyl groups within the molecule exhibit considerable overlap (Fig. 2). The mean perpendicular distance between the groups is *ca* 3.4 Å, so that intramolecular π–π stacking interactions are significant and indeed are possibly the dominant factor underlying the observed conformation; this is almost certainly associated with the fact that the typical interplanar spacing in π–π stacked aromatic systems is very similar to the inter-ring separation in ferrocenes. Furthermore, adjacent molecules are stacked in columns along the [100] direction, such that there are intermolecular π–π stacking interactions between the C2*n* ring in the molecule at (*x*, *y*, *z*) and the ten-membered heteroaromatic ring containing N1 and N4 at (*x* − 1, *y*, *z*), with a mean perpendicular distance between these rings of *ca* 3.5 Å, so that the intra- and intermolecular spacings are very similar. As in 2-ferrocenyl-3-phenylquinoxaline (Glidewell *et al.*, 1996), the neighbouring phenyl and quinoxalinyl groups are nearly normal to one another; the twists of the phenyl groups [76.5 (1) and 77.0 (1)°] away from coplanarity with the quinoxalinyl groups are forced by the presence of the adjacent bulky ferrocenyl group.

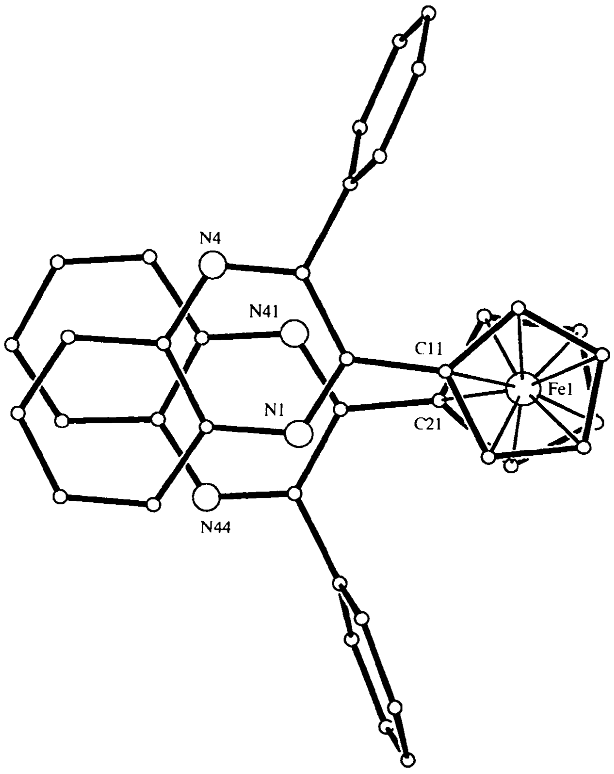

Fig. 2. A view of (I) along the *Cg*1—Fe—*Cg*2 direction, showing the extensive overlap of the two independent quinoxalinyl groups.

Experimental

Equimolar quantities of ferrocene-1,1′-diylbis(2-phenylethanedione), Fe($C_5H_4COCOPh)_2$, and 1,2-diaminobenzene were refluxed in aqueous ethanol in the presence of sodium sulfite and potassium carbonate (Zanello *et al.*, 1998). The organic product was chromatographed on silica, using Et_2O/CH_2Cl_2 (5/95 *v*/*v*) as eluent, to give compound (I) as a crystalline dichloromethane solvate. Analysis: found C 70.8, H 4.3, N 8.4%; $C_{38}H_{26}FeN_4\cdot0.9CH_2Cl_2$ requires C 69.6, H 4.2, N 8.4%; NMR: δ(H) 4.18 (*m*, 4H) and 4.40 (*m*, 4H, 2 × C_5H_4), 7.3–7.8 (*m*, 18H, aromatic); δ(C) 71.1 (*d*), 72.3 (*d*) and 83.8 (*s*) (C_5H_4); 128.2 (*d*), 128.3_6 (*d*), 128.4_3 (*d*), 128.7 (*d*), 128.9 (*d*), 129.1 (*d*), 129.6 (*d*), 138.4 (*s*), 140.2 (*s*), 141.1 (*s*), 151.0 (*s*) and 152.9 (*s*) (phenyl and quinoxalinyl). Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$[Fe(C_{19}H_{13}N_2)_2]\cdot0.9CH_2Cl_2$
$M_r = 670.78$
Triclinic
$P\bar{1}$
$a = 8.3216\,(16)$ Å
$b = 12.392\,(3)$ Å
$c = 15.949\,(2)$ Å
$\alpha = 83.58\,(2)°$
$\beta = 79.634\,(16)°$
$\gamma = 72.990\,(15)°$
$V = 1544.1\,(6)$ Å^3
$Z = 2$
$D_x = 1.443$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.65–18.03°$
$\mu = 0.680$ mm^{-1}
$T = 294\,(1)$ K
Plate
0.42 × 0.28 × 0.01 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*ABSO* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.872$, $T_{max} = 0.990$
5739 measured reflections
5739 independent reflections

2727 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.45°$
$h = -9 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: 1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.144$
$S = 0.852$
5739 reflections
416 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.376$ e Å^{-3}
$\Delta\rho_{min} = -0.273$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C2	1.333 (5)	N41—C42	1.321 (6)
N1—C10	1.362 (6)	N41—C50	1.369 (6)
C2—C3	1.425 (6)	C42—C43	1.443 (6)
C3—N4	1.320 (6)	C43—N44	1.312 (6)
N4—C5	1.376 (6)	N44—C45	1.375 (6)
C5—C6	1.397 (7)	C45—C50	1.395 (7)
C5—C10	1.399 (6)	C45—C46	1.409 (7)
C6—C7	1.359 (7)	C46—C47	1.354 (7)
C7—C8	1.398 (7)	C47—C48	1.409 (8)
C8—C9	1.364 (7)	C48—C49	1.352 (7)
C9—C10	1.411 (7)	C49—C50	1.421 (7)
C2—N1—C10	117.7 (4)	C42—N41—C50	117.5 (4)
C3—N4—C5	117.4 (4)	C43—N44—C45	118.4 (4)
C12—C11—C2—N1	175.2 (5)	C22—C21—C42—C43	176.7 (5)
C15—C11—C2—N1	−0.9 (7)	C25—C21—C42—C43	−0.6 (8)
C12—C11—C2—C3	−3.9 (8)	N41—C42—C43—N44	6.5 (7)
C15—C11—C2—C3	180.0 (5)	C21—C42—C43—N44	−171.7 (5)
N4—C3—C31—C32	−75.3 (6)	N44—C43—C51—C52	−100.8 (6)
C2—C3—C31—C32	106.4 (6)	C42—C43—C51—C52	79.6 (7)
N4—C3—C31—C36	100.7 (6)	N44—C43—C51—C56	71.8 (6)
C2—C3—C31—C36	−77.7 (6)	C42—C43—C51—C56	−107.8 (6)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C61—H61*A*···N44	0.97	2.48	3.292 (9)	141

Compound (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed, and this was confirmed by the analysis. H atoms were treated as riding (C—H 0.93 and 0.97 Å). The common site-occupancy factor of the atoms in the dichloromethane solvate refined to 0.898 (4).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX*96 *via* the Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1238). Services for accessing these data are described at the back of the journal.

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The oxotungsten(IV) complex $[WOCl(Ph_2PCH_2CH_2PPh_2)_2]PF_6\cdot CHCl_3$

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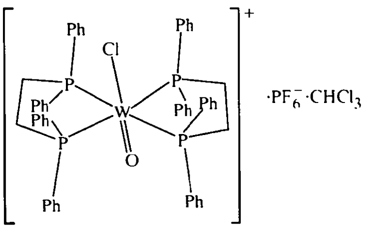
(Received 21 April 1998; accepted 25 November 1998)

Abstract

Crystals of the title compound, chlorobis[ethylenebis(diphenylphosphine-*P*)]oxotungsten(IV) hexafluorophosphate trichloromethane solvate, $[WOCl(C_{26}H_{24}P_2)_2]PF_6\cdot CHCl_3$, contain mononuclear tungsten complex molecules. The W atoms are octahedrally coordinated by two bidentate phosphine ligands and one Cl atom which is located *trans* to an O atom. The W—O distance is 1.851 (3) Å and the mean O—W—P angle is 94 (5)°. In contrast to the reported structure for an analogous cationic tungsten complex, the Cl- and O-atom positions do not show disorder.

Comment

As part of our investigations on tungsten clusters we have prepared the oxotungsten(IV) complex $[WOCl(Ph_2PCH_2CH_2PPh_2)_2]PF_6\cdot CHCl_3$, (1). A satisfactory synthesis of this compound was reported previously by Levason *et al.* (1977), and the complex has been characterized by spectroscopic, magnetic and conductivity measurements. In 1991, Cotton & Mandal reported an X-ray structural study of the tetraphenylborate salt of a similar cationic complex, $[WOCl(Ph_2PCH_2CH_2PPh_2)_2][BPh_4]$, (2), which displays disorder of the O- and Cl-atom positions. The need for more precise data and the general paucity of structural data on oxotungsten(IV) species has led to the work reported here.



(1)

Other structurally characterized mononuclear halogeno-oxotungsten(IV) complexes with phosphino ligands include $[WOCl(Me_2PCH_2CH_2PMe_2)_2]ClO_4$, (3), $[WOCl\{Me_2PCH_2(S)PMe_2\}_2]PF_6$, (4) (Cotton & Llusar, 1988), $[WOBr(Me_2PCH_2CH_2PMe_2)_2]Br\cdot 5H_2O$, (5) (Cotton *et al.*, 1989), and $[WOCl_2(PMePh_2)_2(CH_2{=}CH_2)]$, (6) (Su *et al.* 1986). One common feature of all these systems is the marked oxophilic character of tungsten, which is able to abstract oxygen not only from water but also from organic solvents.

The structures of the cations of (1) and (2) differ significantly in their W—O [1.851 (3) Å for (1) *versus* 1.68 (1) Å for (2)] and W—Cl bond distances [2.408 (1) Å for (1) *versus* 2.53 (1) Å for (2)]. These differences in W—*X* (*X* = O, Cl) bond lengths are likely to have their origin in the Cl/O disorder in (2), as has been discussed by Cotton & Mandal (1991). The importance of crystal purity in the determination of correct bond lengths has been pointed out by Yoon & Parkin (1991). Unusually long Mo—O bonds in oxochloro complexes of molybdenum(IV) have been attributed to disordered structures mainly caused by cocrystallization; this manifests itself in maxima near the oxo position in the difference electron-density maps (Yoon *et al.*, 1991). Difference electron-density maps for compound (1) show no excess electron density close to the O-atom position [in contrast to compound (2)], indicating the absence of disorder in the former crystal, even though a small amount of disorder cannot be ruled out. Also, refinement of the occupancy of the O- and Cl-atom positions results in values very close to unity.

The structure of (1) (Fig. 1) shares common features with those of (2), (3), (4) and (5), and it is closely related to that of (3) with the phosphinomethyl groups replaced by phenyl groups. Among these compounds, (1) has the longest W—O bond distance, 0.17 Å longer than the corresponding distance in (3), and 0.11 Å longer than that of (5). In our opinion, it is not likely that the long W—O bond in (1) is a result of electronic effects because of the similarities of the electronic properties of the ligands in all these compounds. We believe that it is rather the steric effect of the bulkier phosphine that causes the lengthening of the W—O bond.

Because a multiple bond generally occupies more space than a single bond [according to valence-shell electron-pair repulsion (VSEPR) theory], the terminal oxo group in these compounds exerts substantial steric