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Dichloro[ferrocene-1,1′-diylbis(diphenylphosphine-*P*)]mercury(II) Methanol Solvate

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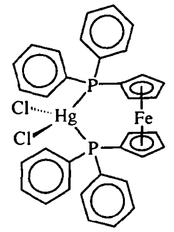
Abstract

The title complex, $[HgCl_2\{Fe(C_{17}H_{14}P)_2\}].CH_3OH$, is monomeric with the Hg atom in a tetrahedral environment provided by the two Cl^- ions and two P atoms of the bis(diphenylphosphino)ferrocene ligand.

Comment

The asymmetric unit contains one $[HgCl_2(dppf)]$, (I), molecule, where dppf is 1,1′-bis(diphenylphosphino)ferrocene, and a disordered methanol solvate molecule. The Hg atom assumes essentially tetrahedral coordination, bonded to the two chelating P atoms of a single 1,1′-bis(diphenylphosphino)ferrocene ligand and to two terminal chloride ions (Fig. 1). The two cyclopentadienyl groups are inclined to each other at an angle of 2.8 (4)° and are tilted away from the Hg^{II} ion. A survey of the other reported complexes of dppf in the Cambridge Structural Database (Allen *et al.*, 1993) shows that the cyclopentadiene rings can adopt eclipsed, staggered and intermediate conformations.



(I)

The geometry appears to be controlled, at least in part, by the size and geometry of the metal ion chelated by the 1,1′-bis(diphenylphosphino)ferrocene ligand. The

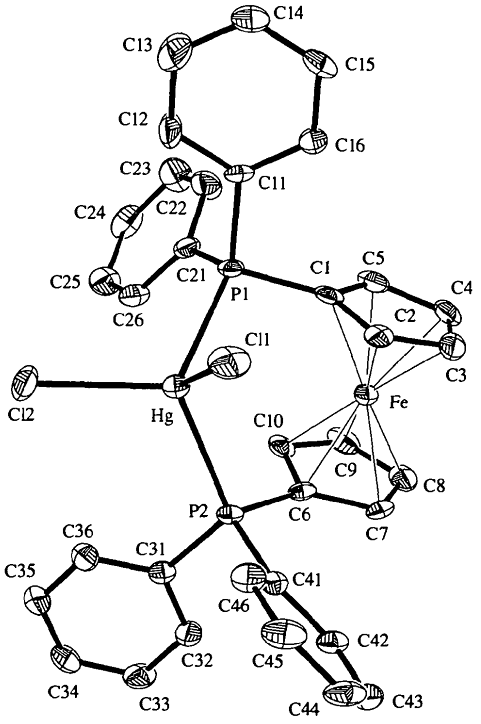


Fig. 1. Perspective view of the title molecule showing 50% probability displacement ellipsoids. H atoms and the disordered methanol have been omitted for clarity.

geometry in which the two P—Cp bonds (Cp is cyclopentadienyl) are eclipsed offers the smallest 'bite' and rotation provides a means of increasing the bite of the chelating ligand. With this in view, the relative conformations of the cyclopentadienyl rings are conveniently described in terms of the angle between the P—Cp bonds, where angles of 0 or $n(360/5)°$ represent eclipsed conformations. The cyclopentadienyl rings are nearly eclipsed (11.7°) in [Ni(dppf)Cl_2] (Casellato *et al.*, 1988), where the small Ni^{II} ion has tetrahedral geometry. However, for the square-planar complexes [Pd(dppf)Cl_2] (Hayashi *et al.*, 1984) and [Pt(dppf)Cl_2] (Butler *et al.*, 1985; De Lima *et al.*, 1995), the geometry is staggered (32.8 and 34.7°, respectively). In the present structure, the P1—C1—C6—P2 torsion angle is −37.8 (3)° demonstrating that a substantial increase in the P···P distance is required to accommodate the large Hg^{II} ion in tetrahedral geometry. As might be expected, the unit-cell packing shows some π–π interactions involving the phenyl rings. Additionally, there are some indications of weak hydrogen bonding between the disordered methanol O atom and the coordinated chloride ions [Cl2···O51 3.21 (1) and Cl1···O52^{i} 3.20 (3) Å; symmetry code: (i) $-x$, $1-y$, $-z$].

Experimental

[$HgCl_2$(dppf)].CH_3OH was prepared by mixing solutions of mercuric chloride (72 mg, 264 mmol) dissolved in 35 ml of methanol with 1,1′-bis(diphenylphosphine)ferrocene (104 mg, 262 mmol) dissolved in 35 ml chloroform. The resulting solution was heated under reflux for 1 h. On cooling, crystalline yellow [$HgCl_2$(dppf)] precipitated immediately in 60% yield. The crystal used for the structure determination crystallized from the mother liquor after isolation of the first crop.

Crystal data

[$HgCl_2\{Fe(C_{17}H_{14}P)_2\}$].-$CH_4O$
$M_r = 856.88$
Triclinic
$P\bar{1}$
$a = 9.835$ (3) Å
$b = 11.403$ (3) Å
$c = 14.717$ (3) Å
$\alpha = 86.75$ (2)°
$\beta = 84.65$ (2)°
$\gamma = 76.07$ (2)°
$V = 1594.0$ (7) Å^3
$Z = 2$
$D_x = 1.785$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 5$–13°
$\mu = 5.561$ mm^{-1}
$T = 153$ (2) K
Block
0.45 × 0.20 × 0.08 mm
Yellow

Data collection

Siemens *P*4 four-circle diffractometer
ω scans from ($K_{\alpha1} - 1$) to ($K_{\alpha2} + 1$)°
Absorption correction: ψ scan (Sheldrick, 1990*b*)
$T_{min} = 0.364$, $T_{max} = 0.641$
6694 measured reflections
5616 independent reflections

4560 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 25°$
$h = -9 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.078$
$S = 1.026$
5616 reflections
385 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.1156P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.10$
$\Delta\rho_{max} = 0.96$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Hg—Cl1	2.5100 (18)	Fe—C7	2.040 (6)
Hg—P1	2.5102 (17)	Fe—C8	2.041 (6)
Hg—P2	2.5162 (16)	Fe—C5	2.044 (6)
Hg—Cl2	2.5281 (18)	Fe—C9	2.046 (6)
Fe—C10	2.028 (6)	Fe—C6	2.048 (6)
Fe—C1	2.033 (6)	Fe—C3	2.055 (7)
Fe—C2	2.039 (6)	Fe—C4	2.055 (6)
Cl1—Hg—P1	99.49 (6)	Cl1—Hg—Cl2	105.78 (6)
Cl1—Hg—P2	109.47 (6)	P1—Hg—Cl2	112.85 (6)
P1—Hg—P2	114.04 (5)	P2—Hg—Cl2	113.83 (6)

The structure was solved by direct methods (*SHELXTL/PC*; Sheldrick, 1990*a*). All the full-occupancy non-H atoms were refined with anisotropic atomic displacement parameters. H atoms were inserted at calculated positions with isotropic displacement parameters riding on U^{ij} of the carrier atoms. The disordered methanol solvate was refined over three possible orientations with the three C—O distances restrained to be similar; these atoms were refined isotropically and the H atoms were not included in the model. Except for some residual electron density in the region of the disordered solvent (highest peak 0.96 e Å^{-3} at 0.66 Å from O51), the final difference map showed no significant features.

Data collection: *XSCANS* (Fait, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1195). Services for accessing these data are described at the back of the journal.

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trans-Diaquabis(4-hydroxybenzoato-*O*)bis(nicotinamide-*N*)copper(II)

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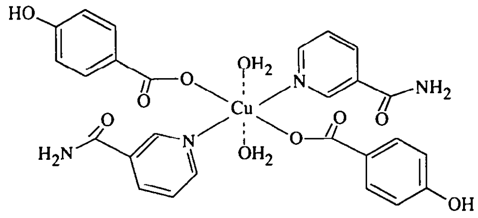
Abstract

The title compound, $[Cu(C_7H_5O_3)_2(C_6H_6N_2O)_2(H_2O)_2]$, is a crystallographically centrosymmetric complex in which pyridine N and carboxylate and water O atoms form a tetragonally Jahn–Teller-distorted octahedron about the Cu^{II} ion with bond distances of 1.956 (2), 2.011 (2) and 2.575 (2) Å. The non-coordinated carboxylate O atoms form hydrogen bonds with the amide N and water O atoms [O···O 2.705 (4) and O···N 2.888(3) Å].

Comment

Nicotinamide (NA) is one form of niacin and a deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). It is thus of interest to determine the manner in which copper interacts with niacin and nicotinamide. The structures of some complexes obtained from the reactions of Cu^{II} ions with nicotinamide have been determined; *e.g.* $[Cu(sal)_2(NA)_2]$ (sal is salicylate) (Hoang *et al.*, 1993) and $[Cu(C_7H_3ClFO_2)_2(NA)_2]$ (Hoang *et al.*, 1995). In these complexes, NA is a monodentate ligand coordinated to Cu^{II} *via* its pyridine N atom. In its rare earth complexes, NA is coordinated to the rare earth ion *via* only the O atoms of the substituents, not by the pyridine N atom (Poray-Koshits *et al.*, 1976). Coordination *via* the amide N atom may also occur. Hence, NA may function as a monodentate or bidentate ligand and may form molecular or polymeric structures affecting such properties of the compounds as their solubility.

For the complex $[Cu(p\text{-}HOC_6H_4COO)_2(H_2O)_3].5H_2O$, Shnulin *et al.* (1981) found a coordination number of five for the Cu^{II} ion. The three coordinated water molecules are located in the symmetry plane and the other two coordination sites are occupied by O atoms belonging to the carboxy groups of the two mirror-imaged acid ligands. The structure of the title molecule, (I), was determined in order to investigate the ligand properties of NA and the *p*-hydroxybenzoate ion, and compare the coordination geometries when the NA ligands are substituted for water in the Shnulin *et al.* (1981) complex.



(I)

The title compound is a monomeric complex with copper at a centre of symmetry. All ligands are monodentate. The pyridine N1 atoms of the two NA ligands and the O1 atoms of the two benzoate ions exhibit slightly distorted square-planar coordination to the Cu atom; the coordination is completed by two water O5 atoms at 2.575 (2) Å to form a tetragonally Jahn–Teller-

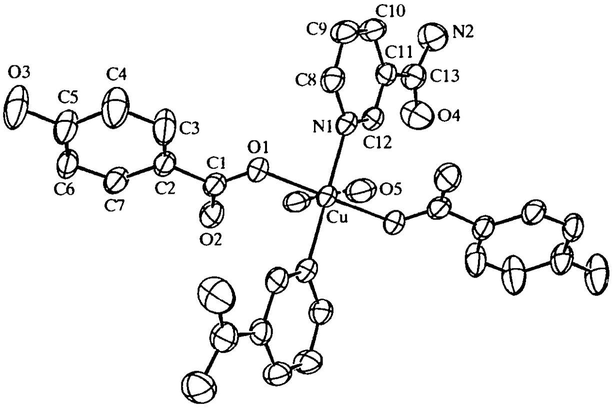


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.