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1,1'-Ferrocenediylbis(2-phenylethanedione): a Three-Dimensional Network Generated by Short C—H...O Hydrogen Bonds

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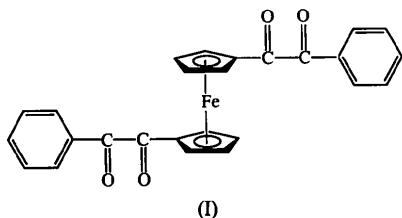
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Abstract

Molecules of ferrocene-1,1'-diylbis(2-phenylethanedione), [Fe(C₁₃H₉O₂)₂], lie across twofold rotation axes. One of the O atoms in each diketone unit acts as an acceptor of two intermolecular C—H...O hydrogen bonds. Hydrogen bonds employing cyclopentadienyl C—H bonds as donors generate spirals of molecules around the 3₁ axes, while those employing phenyl C—H bonds as donors generate two-dimensional sheets.

Comment

Ferrocene-1,2-diketones are important synthetic intermediates and we have recently reported the structure of 1-ferrocenyl-2-phenylethanedione (Glidewell, Gottfried, Trotter & Ferguson, 1996) as a representative example. As part of a wider study of these materials, we now report the structure of a ferrocenediylbis(1,2-diketone) compound, namely 1,1'-ferrocenediylbis(2-phenylethanedione), [Fe(C₅H₄COCOPh)₂], (I).



Compound (I) crystallizes with the molecules lying across twofold rotation axes in the noncentrosymmetric space group *P3₁21*. Examination of the structure with *PLATON* (Spek, 1995a) showed that there were no solvent-accessible voids in the crystal lattice. The C11—C1—O1 fragment is virtually coplanar with the C1_n (*n* = 1–5) cyclopentadienyl ring (Table 2), as found not only in 1-ferrocenyl-2-phenylethanedione (Glidewell, Gottfried, Trotter & Ferguson, 1996), but also in simple acylferrocenes (Gyepes & Hanic, 1975; Sato, Iwai, Sano & Konno, 1984; Barnes, Bell, Glidewell & Howie, 1990).

Similarly, the C21—C2—O2 fragment is almost coplanar with the phenyl ring (Table 2). The mean value of the C1_n—Cg1—Cg1ⁱ—C1(6—*n*ⁱ) torsion angle [*n* = 1–5; Cg1 is the centroid of the cyclopentadienediyl ring; symmetry code: (i) *y*, *x*, *−z*] is $-21.4(1)^\circ$. The corresponding value in 1-ferrocenyl-2-phenylethanedione is $-20.0(4)^\circ$ and both values are essentially midway between the value for complete eclipsing of the rings (0°) and the value for perfect staggering (-36°). The O1—C1—C2—O2 torsion angle is $-120.0(5)^\circ$, which is significantly larger than the values found for both 1-ferrocenyl-2-phenylethanedione [$109.1(5)^\circ$] and benzil (PhCOCOPh) [111.6° ; Brown & Sadanaga, 1965; More, Odou & Lefebvre, 1987], although much less than the value of 180.0° found in the centrosymmetric molecules of butane-2,3-dione (MeCOCOMe) (Eriks, Hayden, Yang & Chan, 1983). The conformation found for (I) has *C*₂ symmetry, so that in the solid state the molecules are chiral. In solution, the NMR spectra indicate that *R*↔*S* interconversion is fast at room temperature, so that crystallization in the *P3₁21* space group represents a case of spontaneous resolution or 'conglomerate crystallization' (Bernal, 1985; Bernal, Cetrullo, Cai & Massoud, 1995).

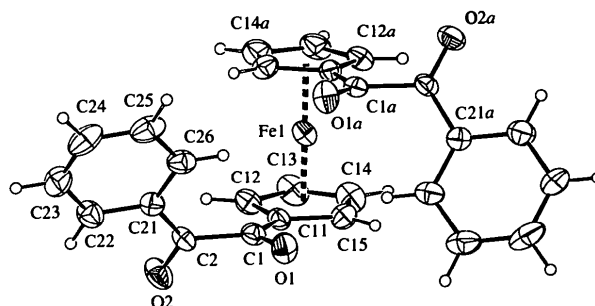


Fig. 1. A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atom labels ending in 'a' have coordinates related by the symmetry transformation (*y*, *x*, *−z*) to those in Table 1.

Each of the two independent O atoms within the molecule of (I) could in principle act as an acceptor of hydrogen bonds and in the absence of other donors hydrogen bonds of type C—H...O may be expected (Hunter, 1991; Hanton, Hunter & Purvis, 1992). There are in fact three types of such interaction (Table 3) having C...O and H...O distances within the accepted criteria for attractive 'soft' hydrogen bonds (Desiraju, 1991; Steiner, 1994; Braga, Grepioni, Biradha, Pedireddi & Desiraju, 1995); atom O1 acts as a single acceptor, while atom O2 acts as an acceptor of two C—H...O hydrogen bonds, rather as the N atom in cyanoferrocene acts as an acceptor of two C—H...N hydrogen bonds (Bell, Ferguson & Glidewell, 1996). Atom O1 in one half of the molecule of (I) acts as an acceptor from

the C26—H26 bond in the other symmetry-related portion of the molecule; there are two such interactions within each molecule, each generating separately a motif characterized by the graph set $S(10)$ and together generating a cyclic motif characterized by the graph set $R_2^2(12)$ (Etter, 1990; Bernstein, Davis, Shimoni & Chang, 1995).

The two interactions involving the O2 atom both have the effect of linking the molecules into continuous networks. The C12—H12 bond in the cyclopentadienyl ring at (x, y, z) acts as a donor to the O2 atom in the fragment at $(x-y, -y, -z-\frac{1}{3})$ and the C12—H12 bond in this fragment acts similarly as a donor to the O2 atom in the fragment at (x, y, z) . This pairwise interaction, which generates a cyclic motif with graph set $R_2^2(12)$, gives rise to a continuous spiral of molecules lying around the 3_1 axis (Fig. 2). In the shorter and presumably stronger C—H...O hydrogen bond, the C24—H24 bond in the phenyl ring at (x, y, z) acts as donor to atom O2 in the fragment at $(-1+x, y, z)$, thus generating a chain motif with graph set $C(7)$. This motif links each molecule to four others and so generates sheets perpendicular to the c direction with successive sheets inter-related by the action of the 3_1 axis (Fig. 3). In 1-ferrocenyl-2-phenylethanedione, the C—H...O hydrogen bonding forms simple chains around a 2_1 axis (Glidewell, Gottfried, Ferguson & Trotter, 1996).

Although an example of a cyclopentadienyl ring acting as a donor in C—H...N hydrogen bonds has been reported recently (Bell, Ferguson & Glidewell, 1996), the behaviour of such rings as donors in C—H...O hydrogen bonds is unusual. The two types of

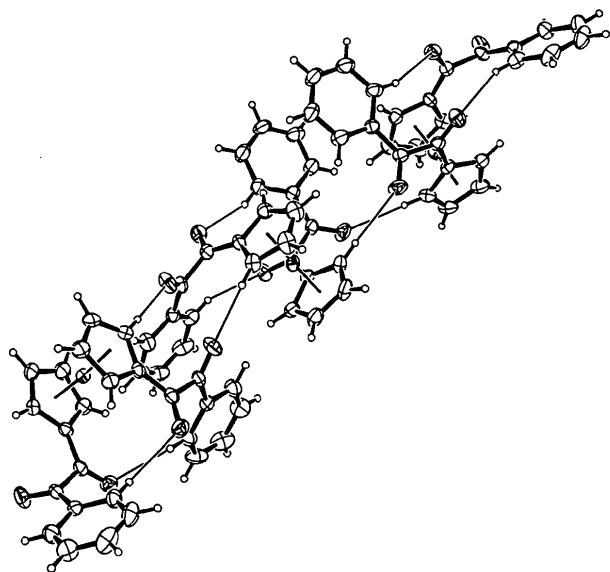


Fig. 2. A view of the hydrogen-bonded 3_1 spirals parallel to the c direction.

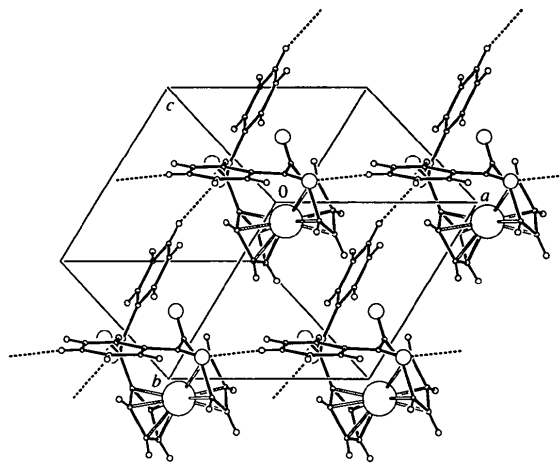


Fig. 3. A view of the hydrogen-bonded sheets that are normal to the c direction.

C—H...O interaction observed here serve to link the molecules into a continuous three-dimensional network.

The adoption by compound (I) of space group $P3_121$ deserves a brief comment. This is not a common space group, with 168 examples among 152 464 entries in the April 1996 release of the Cambridge Structural Database (Allen & Kennard, 1993). An analysis of space-group frequencies in the Cambridge Structural Database (Brock & Dunitz, 1994) has shown that of the space groups having special positions with only twofold rotation symmetry, $P3_121$ exhibits a very high occurrence of $Z' = 0.5$ structures, *i.e.* structures having all the molecules lying across twofold rotation axes, as found here. It was pointed out (Brock & Dunitz, 1994) that twofold rotation axes are particularly effective for bringing molecules with partially concave surfaces into close contact.

Experimental

A sample of compound (I) was prepared by oxidation of 1,1'-bis(phenylacetyl)ferrocene (3.15 g, 7.5 mmol) with manganese(IV) oxide (14.4 g, 165 mmol) in refluxing 1,1,2-trichloroethane (125 ml) for 20 h. Deep-red hexagonal plates were obtained by recrystallization from a dichloromethane/light petroleum solution.

Crystal data

[Fe(C₁₃H₉O₂)₂]

$M_r = 450.25$

Trigonal

$P3_121$

$a = 8.1765(10) \text{ \AA}$

$c = 26.340(2) \text{ \AA}$

$V = 1525.0(2) \text{ \AA}^3$

$Z = 3$

$D_x = 1.471 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 9.75\text{--}14.65^\circ$

$\mu = 0.773 \text{ mm}^{-1}$

$T = 294(1) \text{ K}$

Hexagonal plate

$0.46 \times 0.40 \times 0.26 \text{ mm}$

Red

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: numerical, by Gaussian integration from crystal shape
 $T_{\min} = 0.763$, $T_{\max} = 0.825$
 2949 measured reflections
 1804 independent reflections

1399 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 25^\circ$
 $h = -7 \rightarrow 8$
 $k = -7 \rightarrow 8$
 $l = -30 \rightarrow 31$
 2 standard reflections
 frequency: 120 min
 intensity decay: 2.2%

Refinement

Refinement on F^2
 $R(F) = 0.0487$
 $wR(F^2) = 0.1157$
 $S = 1.065$
 1804 reflections
 140 parameters
 H atoms riding (C—H = 0.93 Å)
 $w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.2136P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.258 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.187 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983)
 Flack parameter = $-0.02(4)$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Fe1	0.1088 (2)		0	0.0460 (3)
O1	-0.2034 (5)	-0.4071 (5)	-0.03856 (12)	0.0636 (10)
O2	-0.0323 (5)	-0.2219 (6)	-0.14854 (11)	0.0741 (12)
C1	-0.0983 (7)	-0.2630 (7)	-0.0617 (2)	0.0457 (11)
C2	-0.1470 (6)	-0.2427 (7)	-0.1170 (2)	0.0461 (12)
C11	0.0816 (6)	-0.1135 (6)	-0.0419 (2)	0.0433 (12)
C12	0.2150 (7)	0.0618 (6)	-0.0647 (2)	0.0513 (12)
C13	0.3626 (7)	0.1602 (8)	-0.0303 (2)	0.067 (2)
C14	0.3239 (7)	0.0553 (9)	0.0144 (2)	0.0659 (14)
C15	0.1505 (7)	-0.1174 (7)	0.0081 (2)	0.0523 (13)
Cg1†	0.2267 (7)	0.0093 (7)	-0.0229 (2)	
C21	-0.3302 (6)	-0.2588 (7)	-0.1287 (2)	0.0458 (11)
C22	-0.3742 (8)	-0.2565 (8)	-0.1796 (2)	0.062 (2)
C23	-0.5391 (8)	-0.2625 (8)	-0.1928 (2)	0.075 (2)
C24	-0.6592 (8)	-0.2689 (9)	-0.1568 (3)	0.084 (2)
C25	-0.6181 (7)	-0.2717 (8)	-0.1057 (2)	0.076 (2)
C26	-0.4528 (7)	-0.2669 (7)	-0.0914 (2)	0.0566 (13)

† Cg1 is the centroid of the C11–C15 ring.

Table 2. Selected geometric parameters (Å , $^\circ$)

Fe1...Cg1	1.655 (4)	C1—C2	1.542 (6)
O1—C1	1.218 (5)	C1—C11	1.460 (6)
O2—C2	1.200 (5)	C2—C21	1.470 (6)
Cg1...Fe1...Cg1 ¹	174.8 (2)	O2—C2—C1	116.4 (4)
O1—C1—C2	118.7 (4)	O2—C2—C21	123.9 (4)
O1—C1—C11	124.0 (4)	C1—C2—C21	119.7 (4)
C2—C1—C11	117.0 (4)		
O1—C1—C2—O2	-120.0 (5)	O1—C1—C11—C15	-2.5 (7)
C11—C1—C2—O2	54.7 (6)	O2—C2—C21—C26	-174.5 (5)
O1—C1—C2—C21	57.0 (6)	O2—C2—C21—C22	2.4 (8)
O1—C1—C11—C12	-179.0 (4)		

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

Table 3. Hydrogen-bonding geometry (Å , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
C12—H12...O2 ⁱⁱ	0.93	2.54	3.469 (6)	178
C24—H24...O2 ⁱⁱⁱ	0.93	2.42	3.267 (9)	152
C26—H26...O1 ⁱ	0.93	2.57	3.454 (6)	159

Symmetry codes: (i) $y, x, -z$; (ii) $x - y, -y, -\frac{1}{3} - z$; (iii) $x - 1, y, z$.

Compound (I) crystallized in the trigonal system; space groups $P3_121$, $P3_221$, $P3_112$ and $P3_212$ are allowed by the Laue symmetry and systematic absences. $P3_121$ was shown to be the correct choice and the Flack (1983) parameter is in agreement with this. The structure was solved by the heavy-atom method.

Data collection: *CAD-4/PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX94*. Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*, *PLATON* (Spek, 1995a) and *PLUTON* (Spek, 1995b). Software used to prepare material for publication: *NRCVAX94*, *SHELXL93* and *WordPerfect* (macro *PREPCIF*).

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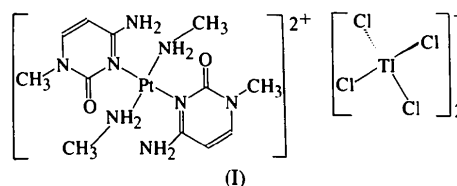
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1133). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Randaccio, Menzer, Danzmann, Holthenrich & Lippert, 1993). The rings of the 1-MeC⁻ ligands bridging the metals present the same orientation with respect to the N—Pt—N vector (a head-to-head arrangement). Attempts at obtaining similar heterobimetallic complexes containing Tl^{III} were unsuccessful and led to the formation of the title compound.



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trans-Bis(methylamine-*N*)bis(1-methylcytosine-*N*³)platinum(II) Bis[tetrachlorothallate(III)]

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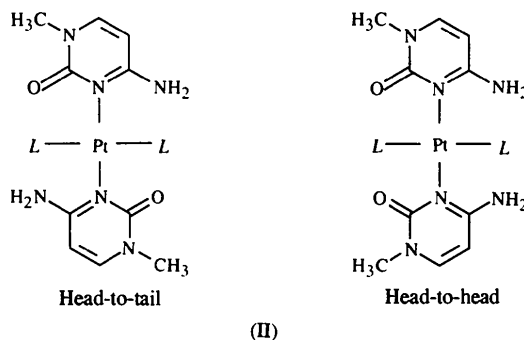
Abstract

The crystal structure of the title compound, *trans*-bis(methylamine-*N*)bis(4-amino-1-methyl-2(1*H*)-pyrimidinone-*N*³)platinum(II) bis[tetrachlorothallate(III)], [Pt(CH₅N)₂(C₅H₇N₃O)₂][TlCl₄]₂, consists of square-planar Pt^{II} cations arranged on a crystallographic inversion center and distorted tetrahedral TlCl₄⁻ anions. The compound is very similar to known cytosine complexes of the *trans*-[(NH₃)₂Pt(1-methylcytosine)₂]*X*₂ type. The distortion in TlCl₄⁻ and in other anion-containing compounds is discussed.

Comment

The title compound, (I), was obtained during our continuing research on the chemistry of heterobimetallic complexes bridged by cytosinate ligands (amino deprotonated, hereinafter 1-MeC⁻). These complexes have the general formulae *trans*-[(NH₃)₂Pt(1-MeC⁻)₂PdL](NO₃)_n (*L* is a neutral or anionic ligand; Krumm, Lippert, Randaccio & Zangrando, 1991; Krumm, Zangrando, Randaccio, Menzer & Lippert, 1993; Mealli, Pichierri, Randaccio, Zangrando, Krumm, Holthenrich & Lippert, 1995) and *trans*-[(NH₃)₂Pt(1-MeC⁻)₂Hg]*X*₂ (*X* is Cl⁻, NO₃⁻; Krumm, Zangrando,

In the complex cation of (I), the Pt atom is positioned on a crystallographic inversion center resulting in a head-to-tail arrangement of cytosine rings (Fig. 1). The Pt—N3 (of 1-MeC) and Pt—N5 (of amine) bond lengths are 2.023 (6) and 2.046 (7) Å, respectively. The coordination around N3 is distorted, with the Pt—N3—C4 angle [121.8 (5)°] significantly larger than the Pt—N3—C2 angle [117.6 (5)°]. The two coplanar 1-MeC ligands are mutually *trans* with respect to rotation about the N3—Pt—N3' vector and form large dihedral angles of 73.9 (2)° with the N₄ coordination plane, possibly for steric reasons. The cation geometry is very similar to that reported for the corresponding bis(amino) complex *trans*-[(NH₃)₂Pt(1-MeC)₂]²⁺ (NO₃⁻ salt: Lippert, Lock & Speranzini, 1981; ClO₄⁻ salt: Brown & Lock, 1988) where the same orientation of the nucleobases has been observed. Although the present Pt complex, when isolated from aqueous solution by slow evaporation, displays the cytosine bases in a head-to-tail arrangement, the corresponding head-to-head rotamer, with the cytosines in the same orientation, has also been isolated (Holthenrich, Sóvágó, Fusch, Erxleben, Fusch, Rombeck & Lippert, 1995).



The geometry of the TlCl₄⁻ anion is characterized by two longer [Tl—Cl1 2.440 (2) and Tl—Cl2 2.421 (3) Å] and two shorter [Tl—Cl3 2.395 (2) and Tl—Cl4 2.402 (2) Å] distances. Correspondingly, the Cl1—Tl—Cl2 and Cl3—Tl—Cl4 angles are 111.2 (1) and 121.9 (1)°, respectively, with the other angles