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An Azomethylene Carbonyliron Complex from 4,4′-Dimethylbenzaldazine, μ_2,η^2,σ^3-(4-Methylbenz-1-al)hydrazone-N^1-(5-methylbenzylidene)hexacarbonyldiiron†

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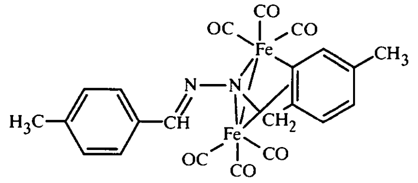
Abstract

The crystal structure of the title complex, $[Fe_2(C_{16}H_{16}N_2)(CO)_6]$, contains two crystallographically independent molecules of the complex which have enantiomeric conformations and show notable differences in the geometry of the organic ligand. The typical Fe—Fe single bond is unsymmetrically bridged by the N atom and by a 3-metallated 2,3-π bonded aromatic ring.

Comment

The structure of the title compound, (I), was determined as part of a study on the structural chemistry of carbonyliron complexes obtained from azines $(R^1R^2$-C=N-$)_2$ and iron carbonyls (Zimniak & Buczkowski, 1980,1982; Zimniak, 1992). In reactions of ketazines, the central N—N bond is cleaved and bis(μ-iminato)–bis(tricarbonyliron) complexes have been formed with a tetrahedral central core (Bright & Mills, 1967). In our previous work, a complex of this type with R^1 = Ph and R^2 = CH_3 was reported for the first time in the form of two structural *anti* and *syn* isomers (Zimniak & Zachara, 1997).



(I)

In contrast to this, the type of substitution on the aldazine system is critical for the path of complexation. A complex of an aliphatic aldazine $[Fe_2(CO)_6(CH_3CHN)_2]$ has been reported as a typical di-μ-iminato system occurring in the *syn*-form only (Gervasio *et al.*, 1981). In the complex of benzaldazine (PhCH=N-$)_2$, the backbone of the molecule remains intact, the reaction occurs with *ortho*-proton rearrangement to the azomethine C atom and the metallization of the phenyl ring (Nametkin *et al.*, 1986). In order to determine the effect of *para*-ring substitution on the structure, a series of complexes of this type of aldazine, (p-RPhCH=N-$)_2$ (R = F, CH_3, OCH_3), has been obtained (Zimniak, 1992). The results of the X-ray structure investigation of the *para*-methyl derivative are the subject of this paper.

The title complex was synthesized by the reaction of triiron dodecacarbonyl with 4,4′-dimethylbenzaldazine, following a previously described procedure (Zimniak, 1992). The X-ray study reveals that the monoclinic unit cell contains two crystallographically independent molecules of the complex with enantiomeric conformations. The general folding of both molecules (I) and (I′) is similar and consistent with the type of structure described for the complex derived from unsubstituted benzaldazine (Nametkin *et al.*, 1986). As shown in Fig. 1, the typical iron–iron single bond [Fe1—Fe2 2.4224 (10) and Fe1′—Fe2′ 2.4176 (9) Å] is unsymmetrically double bridged by the nitrogen (N1 and N1′) atom and by a 3-metallated 2,3-π bonded aromatic ring (C16 and C16′), forming a central core of the complex. Only small differentiation of the Fe—N—Fe σ bonds has been observed [1.963 (3) and 1.952 (3) Å for (I), and 1.965 (2) and 1.952 (2) Å for (I′)]. In contrast, an asymmetric Fe—(aromatic ring)—Fe bridge is formed by a σ bond [Fe1—C16 1.979 (4) Å

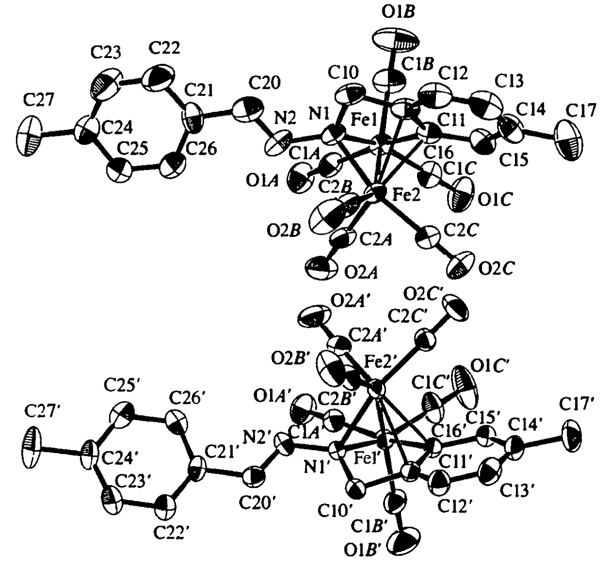


Fig. 1. *ORTEP*III (Burnett & Johnson, 1996) plot of molecules (I) and (I′) with the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

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† Alternative name: hexacarbonyl-1κ^3C,2κ^3C-[μ-4-methylbenzaldehyde 4-methylbenzyl-1κN^1,1κC^2:2κN^1,2(1,2-η)-hydrazone]diiron(*Fe—Fe*).

and Fe1′—C16′ 1.991 (3) Å] which is located in a plane of the aromatic ring and of the π-coordination of the aromatic C—C bond [Fe2—C16 2.160 (3) and Fe2—C11 2.372 (4) Å, and Fe2′—C16′ 2.165 (3) and Fe2′—C11′ 2.388 (3) Å]. Considering the short contact between Fe2 (Fe2′) and C10 (C10′) [2.658 (4) and 2.677 (3) Å] extension of the π donation from the system C10—C11—C16 (C10′—C11′—C16′) cannot be ruled out.

Noticeable differences in the geometry of organic ligands between (I) and (I′) are observed only in their central regions. The N—N bond in (I′) [1.409 (3) Å] is substantially shorter than that in (I) [1.468 (4) Å], whereas the remaining bonds in the C11′–C21′ chain are lengthened compared to those in (I). Differences have been also noted in the values of a number of respective valence and torsion angles, *e.g.* N1—N2—C20—C21 in (I) [179.2 (3)°] is greater than N1′—N2′—C20′—C21′ in (I′) [173.4 (3)°]. Nevertheless, the dihedral angle defined by the planes of the two aromatic rings are almost the same [50.4 (1) and 50.7 (1)° for (I) and (I′), respectively]. The shortest intermolecular distances involve O atoms [O2*C*···O2*A*′$(x-1, y, z)$ 2.997 (4) and O2*B*′···O2*C*′$(-x+2, y+\frac{1}{2}, -z+\frac{1}{2})$ 3.045 (4) Å] and between C atom C20′ in (I′) and O atom O2*C*′$(-x+2, y+\frac{1}{2}, -z+\frac{1}{2})$ 3.054 (5) Å.

Experimental

The title compound was prepared according to the procedure described previously (Zimniak & Buczkowski, 1980), followed by recrystallization from *n*-hexane solution at ambient temperature; m.p. 383–385 K.

Crystal data

$[Fe_2(C_{16}H_{16}N_2)(CO)_6]$
$M_r = 516.07$
Monoclinic
$P2_1/c$
$a = 8.839 (3)$ Å
$b = 13.858 (3)$ Å
$c = 37.155 (12)$ Å
$\beta = 92.51 (3)°$
$V = 4547 (2)$ Å^3
$Z = 8$
$D_x = 1.508$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31 reflections
$\theta = 7.77–17.15°$
$\mu = 1.316$ mm^{-1}
$T = 293 (2)$ K
Prismatic
0.70 × 0.60 × 0.30 mm
Dark red

Data collection

Siemens *P*3 diffractometer
Profile data from ω–2θ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.565$, $T_{max} = 0.713$
6998 measured reflections
6511 independent reflections
4891 reflections with $I > 2\sigma(I)$

$R_{int} = 0.021$
$\theta_{max} = 23.55°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = -41 \rightarrow 41$
2 standard reflections every 70 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.081$
$S = 1.024$
6500 reflections
594 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.6895P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.00037 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Fe1—Fe2	2.4224 (10)	Fe1′—Fe2′	2.4176 (9)
Fe1—N1	1.963 (3)	Fe1′—N1′	1.965 (2)
Fe1—C16	1.979 (4)	Fe1′—C16′	1.991 (3)
Fe2—N1	1.952 (3)	Fe2′—N1′	1.952 (2)
Fe2—C16	2.160 (3)	Fe2′—C16′	2.165 (3)
Fe2—C11	2.372 (4)	Fe2′—C11′	2.388 (3)
Fe1—C1*A*	1.823 (4)	Fe1′—C1*A*′	1.809 (4)
Fe1—C1*B*	1.761 (5)	Fe1′—C1*B*′	1.759 (4)
Fe1—C1*C*	1.766 (4)	Fe1′—C1*C*′	1.763 (4)
Fe2—C2*A*	1.751 (4)	Fe2′—C2*A*′	1.746 (4)
Fe2—C2*B*	1.793 (4)	Fe2′—C2*B*′	1.794 (4)
Fe2—C2*C*	1.793 (4)	Fe2′—C2*C*′	1.786 (4)
N1—N2	1.468 (4)	N1′—N2′	1.409 (3)
N1—C10	1.448 (4)	N1′—C10′	1.466 (4)
N2—C20	1.206 (5)	N2′—C20′	1.229 (4)
C10—C11	1.495 (5)	C10′—C11′	1.502 (4)
C11—C16	1.410 (5)	C11′—C16′	1.399 (4)
C20—C21	1.466 (6)	C20′—C21′	1.478 (4)
N1—Fe1—C16	77.89 (14)	N1′—Fe1′—C16′	77.80 (11)
N1—Fe2—C16	73.92 (13)	N1′—Fe2′—C16′	74.02 (10)
N1—Fe2—C11	62.56 (13)	N1′—Fe2′—C11′	62.49 (10)
N2—N1—C10	120.8 (3)	N2′—N1′—C10′	120.0 (2)
N2—N1—Fe2	118.3 (2)	N2′—N1′—Fe2′	117.3 (2)
C10—N1—Fe2	101.8 (2)	C10′—N1′—Fe2′	102.2 (2)
N2—N1—Fe1	117.3 (2)	N2′—N1′—Fe1′	118.8 (2)
C10—N1—Fe1	112.9 (2)	C10′—N1′—Fe1′	113.0 (2)
Fe2—N1—Fe1	76.46 (10)	Fe2′—N1′—Fe1′	76.21 (8)
C20—N2—N1	118.9 (4)	C20′—N2′—N1′	119.4 (3)
N1—C10—C11	101.2 (3)	N1′—C10′—C11′	100.5 (2)
C16—C11—C10	114.5 (3)	C16′—C11′—C10′	115.5 (3)
C11—C16—Fe1	113.4 (3)	C11′—C16′—Fe1′	113.4 (2)
C11—C16—Fe2	80.3 (2)	C11′—C16′—Fe2′	81.1 (2)
Fe1—C16—Fe2	71.51 (12)	Fe1′—C16′—Fe2′	71.01 (10)
N2—C20—C21	119.2 (5)	N2′—C20′—C21′	120.8 (3)

Since the absorption coefficient was comparatively high, a correction based on a well defined crystal shape was applied using *SHELX*76 (Sheldrick, 1976). The phase problem was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). H atoms were introduced at idealized positions with isotropic displacement parameters.

Data collection: *P*3/*P*4-*PC Diffractometer Program* (Siemens, 1991*a*). Cell refinement: *P*3/*P*4-*PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991*b*). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *PARST*96 (Nardelli, 1995) and *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1358). Services for accessing these data are described at the back of the journal.

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Dichloro[(−)-sparteine-*N*,*N*′]copper(II)

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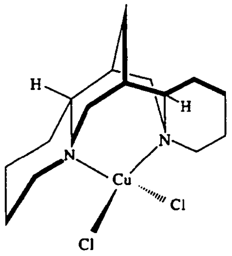
Abstract

In the title compound, [CuCl$_2$(C$_{15}$H$_{26}$N$_2$)], the bulky fused rings of the sparteine ligand induce a pseudo-tetrahedral environment around the copper(II) atom. All four alkaloid rings adopt the chair conformation, with one terminal ring inclined *endo* (pointing towards the metal atom) and the other inclined *exo* (pointing away from the metal). The main dimensions of the complex include Cu—N 2.003 (3) and 2.021 (3), Cu—Cl 2.238 (1) and 2.258 (1) Å, N—Cu—N 90.5 (2) and Cl—Cu—Cl 106.92 (6)°.

Comment

Metal complexes of sparteine alkaloids (Mason & Peacock, 1973) are useful reagents in organic synthesis. The bulky chiral sparteine ligand creates asymmetry around the metal atom, and can induce varying degrees of enantiomeric purity when used in certain addition reactions (Beak *et al.*, 1996; Kretchmer, 1972). The exact geometry of the complexes, and in particular the steric accessibility to the metal center, is the key to their successful application. The current compound, (I), was isolated during our ongoing study of copper-catalyzed asymmetric zinc addition reactions (Jansen & Feringa, 1990; Ukaji *et al.*, 1996).



(I)

The four-ring natural alkaloid (−)-sparteine has two additional diastereomers, α-isosparteine and β-isosparteine, which are distinguished by the different orientations of their two terminal rings (Boschmann *et al.*, 1974). The crystal structure of the Cu^{II} chloride adduct of β-isosparteine has been reported previously (Childers *et al.*, 1975), in which the ligand retains its original conformation when coordinated to the metal. The structures of the other two isomeric metal complexes have only been postulated from various spectroscopic (Choi *et al.*, 1975) and reactivity data (Cady *et al.*, 1977) of copper(II)–sparteine complexes, indicating the retention of conformation when each isomer chelates to metal cations.

A view of the molecular structure of the title compound is shown in Fig. 1. Copper(II) metal centers typically display an octahedral (Jahn–Teller distorted) coordination geometry. However, in both the copper complex of β-isosparteine (Childers *et al.*, 1975) and the present structure, the steric bulk of the bidentate sparteine ligand and the chloride anions lowers the coordination number to four, with a very compressed N—Cu—N angle of 90.5°. In addition, the tetrahedron is twisted, thereby further distorting the bond angles. The Cl1—Cu—Cl2 angle in Fig. 1 is 106.92 (6)°, close to the 109.5° angle in a perfect tetrahedron. All of the other angles about the copper(II) center deviate substantially from ideal [from 100.05 (11) to 134.13 (11)°]. The distorted coordination geometry is very similar to the dimethylzinc complex of (−)-sparteine (Motevalli *et al.*, 1993).

As predicted by previous investigators, the conformation of the dichloro[(−)-sparteine]copper(II) complex consists of one terminal ring folded down over the metal