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Di-μ_2-carbonyl-octacarbonyl[μ_2-η^2,η^2-*N*-cyclohexyl-*N*-(2-thienylmethylene)amine]tetrairon(0)

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In the title compound, [$Fe_4(C_{11}H_{14}NS)_2(CO)_{10}$], the four Fe atoms show a non-linear arrangement with a planar central $Fe_2(\mu_2\text{-}CO)_2$ core. The imine ligands are situated on the same side of the transition metal chain with the N atoms in a *trans* configuration with respect to each other.

Key indicators

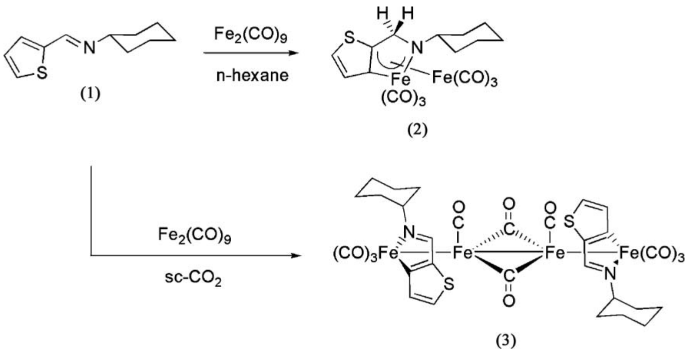
Single-crystal X-ray study
T = 213 K
Mean σ(C–C) = 0.011 Å
R factor = 0.066
wR factor = 0.136
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The coordination chemistry of α,β-unsaturated imine ligands towards group 8 transition metals has been studied intensively in the past decades because these compounds might help explain the initial steps of catalytic C—H activation or C—C bond formation processes of the same ligands catalyzed mostly by ruthenium compounds (Elsevier *et al.*, 1992, and references therein; Imhof, 1996,1997*a*,*b*, 1999; Imhof, Göbel, Braga *et al.*, 1999, and references therein; Imhof, Göbel, Ohlmann *et al.*, 1999; Imhof & Göbel, 2000; Imhof, Göbel, Schweda, Dönnecke & Halbauer, 2005; Imhof, Göbel, Schweda & Görls, 2005; Göbel *et al.*, 2003).

The scheme below shows the synthesis of the title compound, (3). The imine ligand (1) derived from thiophene-2-carbaldehyde and cyclohexylamine reacts with $Fe_2(CO)_9$ in *n*-hexane regioselectively *via* a C—H activation in the 3-position of the thiophene ring leading to the isolation of a dinuclear iron carbonyl compound in 52% yield (Imhof, 1997*a*). During the formation of (2) the H atom that was bound in the 3-position of the heterocycle is transferred to the former imine C atom, generating a methylene group instead. The fact that this C—H activation hydrogen transfer reaction sequence is a strictly intramolecular reaction pathway has been shown for selectively deuterated benzaldimine derivatives (Imhof, Göbel, Ohlmann *et al.*, 1999). When we performed the same reaction in supercritical carbon dioxide, in which $Fe_2(CO)_9$ is soluble, we observed the formation of (3) as the only iron carbonyl complex in low yield together with a large amount of unreacted (1).



The molecular structure of (3) is depicted in Fig. 1. It has been pointed out before that tetranuclear compounds of this kind are isolobally related to $[CpFe(CO)_2]_2$ because of the azaferracyclopentadienyl fragments which are isolobal to Cp^- (Elsevier *et al.*, 1992; Imhof, 1996). It has also been demonstrated that, in principle, four different stereoisomers of (3) might exist depending on the question of whether the imine ligands are situated on the same side of the tetranuclear transition metal chain and, in addition, whether the imine ligands show a *cis*- or *trans*-arrangement relative to each other. Adopting the nomenclature that Elsevier *et al.* (1992) introduced for ruthenium analogues of (3), the title compound would best be described as a *cis*-(*AA*) isomer. Since the *cis*-(*AA*) stereoisomers belong to the point group *C*2 the compounds are chiral. Nevertheless, in the crystal structure of (3) both enantiomers are present due to the crystallographic center of inversion. There have been reports concerning the molecular structures of three more compounds showing the same *cis*-(*AA*) arrangement in the crystalline state (Tzeng *et al.*, 2003; Mul *et al.*, 1993; Beers *et al.*, 1993), although the structure presented by Beers *et al.* is not really comparable because there are no bridging carbon monoxide ligands and the structure therefore should be much more flexible. In addition, there are four more structurally characterized derivatives adopting a *trans*-(*AC*) (Polm *et al.*, 1988; Imhof, 1996) or *trans*-(*AA*) (Imhof, 1999; Mul *et al.*, 1991) conformation.

The bond lengths and angles in (3) are comparable to the values determined for the above-mentioned derivatives. The central metal–metal bond (Fe2—Fe3) is about 0.08 Å longer than Fe1—Fe2 and Fe3—Fe4. As expected, the iron–nitrogen and iron–carbon bond lengths inside the azaferracyclopentadienyl ligands (Fe4—N1, Fe1—N2, Fe4—C3 and Fe1—C14) are significantly shorter than the corresponding bonds of the central Fe atoms towards N or C atoms of the azaferracyclopentadienyl groups (Fe3—N1, Fe3—C3, Fe2—N2 and Fe2—C13). In addition, the iron–carbon bond lengths from Fe2 or Fe3, respectively, involving the C atoms of the ligands are not identical. For both subunits the iron–carbon bond for the C atoms next to the N atoms (C5 and C16) are the shortest of these bonds whereas the bonds with the thiophene C atoms (C3, C4 and C14, C15) formally representing a side-on coordinated carbon–carbon double bond are about 0.1 Å longer.

The central $Fe_2(\mu\text{-}CO)_2$ unit is almost planar with deviations from the mean plane of *ca* 0.14 Å. The azaferracyclopentadienyl ligands are also nearly perfectly planar, with deviations of 0.01–0.08 Å for Fe1/N2/C16/C15/C14 and of 0.01–0.03 Å for Fe4/N1/C5/C4/C3.

Experimental

A 300 mg sample of $Fe_2(CO)_9$ (0.82 mmol) was placed in an autoclave together with (1) (200 mg, 1 mmol) under inert conditions. Afterwards the cooled autoclave was pressurized with carbon dioxide and the temperature was then raised to 314 K to reach the supercritical conditions for carbon dioxide. After 24 h, the autoclave was cooled, the pressure was released and the brown solid residue was dissolved in anhydrous dichloromethane. This solution was transferred to a chromatography column where the product mixture was separated. Elution with light petroleum (b.p. 312-332 K) produced a yellow band with 180 mg of unreacted (1). Another brown band was obtained using a mixture of light petroleum and dichloromethane (3:1) as the eluant. Evaporation of solvent led to the isolation of red–brown microcrystalline (3) (46 mg, 0.05 mmol, 12%).

Crystal data

$[Fe_4(C_{11}H_{14}NS)_2(CO)_{10}]$
$M_r = 888.08$
Orthorhombic, *Pbca*
$a = 21.924$ (4) Å
$b = 13.520$ (2) Å
$c = 23.743$ (4) Å
$V = 7038$ (2) Å^3
$Z = 8$
$D_x = 1.676$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 1.79$ mm^{-1}
$T = 213$ (2) K
Cuboid, red–brown
0.2 × 0.2 × 0.07 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.725$, $T_{\max} = 0.886$
8715 measured reflections
7277 independent reflections
3568 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.069$
$\theta_{\max} = 26.5°$
3 standard reflections
frequency: 60 min
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.136$
$S = 0.99$
7277 reflections
452 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—C14	1.955 (7)	S2—C15	1.741 (7)
Fe1—N2	1.998 (5)	C1—C2	1.336 (10)
Fe1—Fe2	2.4945 (14)	C1—S1	1.728 (8)
Fe2—N2	2.050 (5)	C2—C3	1.451 (9)
Fe2—C16	2.126 (7)	C3—C4	1.383 (9)
Fe2—C14	2.216 (7)	C4—C5	1.420 (8)
Fe2—C15	2.241 (7)	C4—S1	1.746 (7)
Fe2—Fe3	2.5625 (13)	C5—N1	1.356 (7)
Fe3—N1	2.083 (5)	N1—C6	1.503 (7)
Fe3—C5	2.135 (6)	C12—C13	1.338 (10)
Fe3—C4	2.209 (7)	C13—C14	1.427 (9)
Fe3—Fe4	2.4819 (13)	C14—C15	1.410 (9)
Fe4—C3	1.934 (7)	C15—C16	1.404 (9)
Fe4—N1	1.994 (5)	C16—N2	1.355 (8)
S2—C12	1.733 (8)	N2—C17	1.495 (8)
C14—Fe1—N2	81.1 (3)	C4—C3—C2	110.3 (7)
N2—Fe2—Fe3	142.67 (16)	C4—C3—Fe4	114.5 (5)
C16—Fe2—Fe3	112.24 (19)	C3—C4—C5	116.4 (6)
C14—Fe2—Fe3	120.67 (17)	C3—C4—S1	112.9 (5)
C15—Fe2—Fe3	104.72 (18)	N1—C5—C4	112.0 (6)
Fe1—Fe2—Fe3	164.40 (5)	C5—N1—Fe4	116.1 (4)
N1—Fe3—Fe2	140.56 (15)	C1—S1—C4	89.7 (4)
C5—Fe3—Fe2	111.58 (18)	C13—C12—S2	112.8 (6)
C4—Fe3—Fe2	106.81 (18)	C12—C13—C14	115.3 (7)
C3—Fe3—Fe2	125.43 (18)	C15—C14—C13	108.8 (6)
Fe4—Fe3—Fe2	167.87 (5)	C15—C14—Fe1	112.9 (5)
C3—Fe4—N1	80.7 (2)	C16—C15—C14	115.7 (6)
C12—S2—C15	90.0 (4)	C14—C15—S2	113.2 (5)
C2—C1—S1	114.1 (6)	N2—C16—C15	114.1 (6)
C1—C2—C3	112.8 (7)	C16—N2—Fe1	114.9 (4)

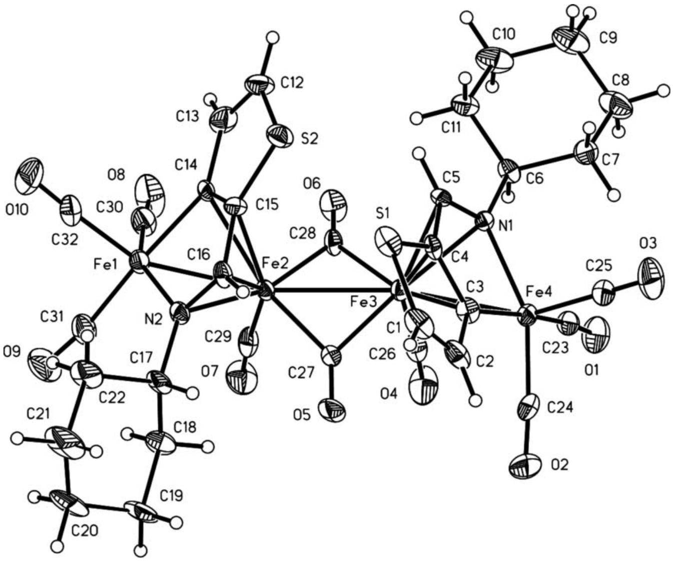


Figure 1
Molecular structure of the title compound. Displacement parameters are drawn at the 40% probability level.

All H atoms were placed in idealized positions (C—H = 0.94–0.99 Å) and treated as riding; the $U_{\rm iso}$(H) value was set to 1.5$U_{\rm eq}$ of the corresponding parent atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* (Boer *et al.*, 1984); data reduction: *MolEN* (Enraf–Nonius, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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