

In (1), the H and Cl atoms of the CH₂Cl₂ solvent molecule are disordered over two sites, with fractional site occupancies of 0.84 and 0.16. Similarity restraints were applied to all four C—Cl distances to keep the geometry of the solvent molecule reasonable; this requirement, together with the refined U_{ij} values, indicates that the disorder model is only approximate.

For both compounds, data collection: *SMART* (Siemens, 1995a); cell refinement: *SAINT* (Siemens, 1995a); data reduction: *SAINT*; program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *SHELXTL* (Siemens, 1995b); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1328). Services for accessing these data are described at the back of the journal.

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Acetylferrocene thiosemicarbazone

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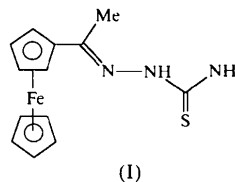
(Received 29 April 1999; accepted 9 August 1999)

Abstract

The thiosemicarbazone moiety of the title compound, [Fe(C₅H₅)(C₈H₁₀N₃S)], shows an *E* configuration and exists in the thione tautomeric form. The molecules are linked together by a pair of N—H···S hydrogen-bonding interactions to form an infinite chain.

Comment

There is considerable interest in non-linear optical materials because of their potential use in device applications related to telecommunications, optical computing, optical storage and optical information processing (Williams, 1984; Chemla & Zyss, 1987; Long, 1995). The polarizability and hyperpolarizability of ferrocene and its derivatives have been the subject of some recent studies (Green *et al.*, 1987; Togni & Rihs, 1993; Ghoshal *et al.*, 1990). As part of our work in this area (Tian *et al.*, 1997; Duan *et al.*, 1998), we report here the structure of the title compound, (I).



The thiosemicarbazone moiety of (I) (Fig. 1) shows an *E* configuration about both the C2—N3 and C1—N2 bonds, as found in most thiosemicarbazides and thiosemicarbazones. The C—S bond distance of 1.693 (3) Å agrees very well with those in related compounds, being intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a double bond (Sutton, 1965). The shortening of the N—N bond distance of 1.387 (4) Å, compared with the corresponding N—N distance of 1.411 (2) Å for unsubstituted thiosemicarbazide (Andretti *et al.*, 1970), indicates that there is delocalized character in the whole molecule.

The intermolecular hydrogen bonds that link the molecules together in the crystal feature an infinite chain consolidated by hydrogen bonds of the type N1—H1N···S1¹ [symmetry code: (i) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$],

with an N...S separation of 3.388 (3) Å and an N1—H1NB...S1¹ angle of 167 (4)°.

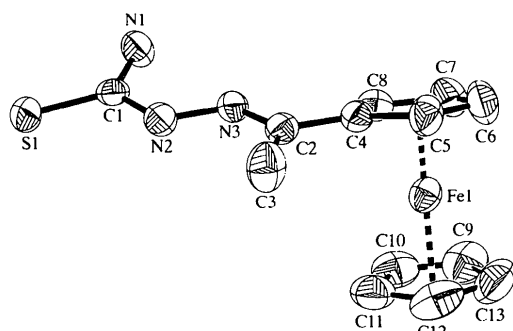


Fig. 1. ORTEP (Johnson, 1965) plot of the title complex showing 35% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

The title compound was synthesized by refluxing a methanol solution (30 ml) of acetylferrocene (0.46 g, 2 mmol) and thiosemicarbazide (0.18 g, 2 mmol) for 2 h. The orange crystalline solid formed was isolated and dried under vacuum. Good quality crystals of (I) were obtained by evaporating a dichloromethane solution in air.

Crystal data

[Fe(C₅H₅)(C₈H₁₀N₃S)]

$M_r = 301.19$

Monoclinic

$P2_1/n$

$a = 11.793 (7) \text{ \AA}$

$b = 7.766 (2) \text{ \AA}$

$c = 14.926 (4) \text{ \AA}$

$\beta = 96.65 (4)^\circ$

$V = 1357.8 (9) \text{ \AA}^3$

$Z = 4$

$D_x = 1.473 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 31 reflections

$\theta = 5.34\text{--}10.04^\circ$

$\mu = 1.25 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Block

$0.6 \times 0.4 \times 0.4 \text{ mm}$

Orange

Data collection

Siemens P4 diffractometer

$2\theta/\omega$ scans

Absorption correction:

empirical via ψ scan

(North *et al.*, 1968)

$T_{\min} = 0.50$, $T_{\max} = 0.59$

3173 measured reflections

2376 independent reflections

2058 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 25^\circ$

$h = -1 \rightarrow 14$

$k = -1 \rightarrow 9$

$l = -17 \rightarrow 17$

3 standard reflections

every 97 reflections

intensity decay: 3.9%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.126$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.09 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$

$S = 1.085$

2371 reflections

224 parameters

All H-atom parameters

refined

$w = 1/[\sigma^2(F_o^2) + (0.0710P)^2 + 0.8636P]$

where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:

SHELXL97 (Sheldrick, 1997)

Extinction coefficient:

0.002 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|----------|-----------|----------|-----------|
| Fe1—C9 | 2.030 (4) | Fe1—C7 | 2.049 (4) |
| Fe1—C5 | 2.036 (3) | Fe1—C11 | 2.053 (4) |
| Fe1—C12 | 2.038 (4) | S1—C1 | 1.693 (3) |
| Fe1—C13 | 2.038 (4) | N1—C1 | 1.315 (4) |
| Fe1—C4 | 2.038 (3) | N2—C1 | 1.345 (4) |
| Fe1—C8 | 2.041 (4) | N2—N3 | 1.387 (4) |
| Fe1—C10 | 2.042 (4) | N3—C2 | 1.290 (4) |
| Fe1—C6 | 2.048 (4) | | |
| C1—N2—N3 | 118.2 (3) | N2—C1—S1 | 120.1 (2) |
| C2—N3—N2 | 116.9 (3) | N3—C2—C4 | 115.6 (3) |
| N1—C1—N2 | 117.0 (3) | N3—C2—C3 | 125.2 (3) |
| N1—C1—S1 | 122.8 (2) | C4—C2—C3 | 119.3 (3) |

All H atoms were refined and C—H distances are in the range 0.87 (5)—0.97 (4) Å.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965) in *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1482). Services for accessing these data are described at the back of the journal.

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[*N,N'*-Bis(salicylidene)ethylenediaminato-*N,N',O,O'*]platinum(II)

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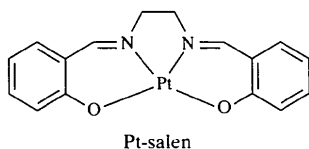
(Received 17 February 1999; accepted 5 August 1999)

Abstract

The title compound, [Pt(C₁₆H₁₄N₂O₂)], is nearly planar. There is pairing of two molecules with a Pt···Pt distance of 3.277(1) Å indicating weak interaction. The pairs form puckered layers in the (010) planes.

Comment

A great number of structures of Schiff base complexes of divalent first row transition metal ions are well known. They exhibit either planar (Akhtar & Drew, 1982) or tetrahedral (Fox *et al.*, 1964) coordination around the central atom. Also, widening of the coordination sphere by additional metal–metal (Shkol'nikova *et al.*, 1970) or metal–base (Hall *et al.*, 1968) interactions can occur. No complete structural data of heavier transition metals, especially of group ten metals, are known so far. Only the point group and unit-cell dimensions of the Pd–salen complex have been reported (Shkol'nikova *et al.*, 1963), though this complex exhibits interesting catalytic properties (Henrici-Olivé & Olivé, 1974). The structure of Pt–salen described here is the first one reported for this type of complex.



The whole molecule is nearly planar with a hardly perceptible arch-like deviation from the long axis (Fig. 1). The tetrahedral distortion around the Pt ion is very small, as indicated by the deviations of the ligating atoms from the best plane defined by them: O1 0.015(2), O2 –0.015(2), N1 –0.016(2) and N2 0.016(2) Å. The Pt atom deviates by 0.007(2) Å and the maximum deviation from the plane is shown by C15 [0.373(9) Å], giving the PtN₂(CH₂)₂ ring an envelope form.

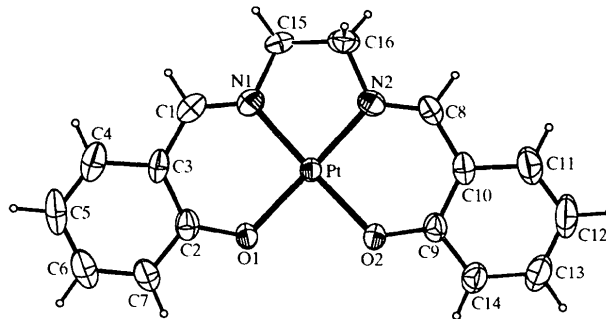


Fig. 1. The molecular structure of Pt–salen showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The arrangement of the molecules within the crystal lattice (Fig. 2) is in pairs with a rotation of 180° and a Pt···Pt distance of 3.277(1) Å indicating metal–metal interaction as in the analogous Ni–salen complex (3.21 Å; Gaetani Manfredotti & Guastini, 1983). These pairs form puckered layers with an alternate tilt angle of ±24.4(3)° from the (010) plane. The analogy of the lattice constants of Pd–salen to Pt–salen suggests a similarity of the structures with only slightly different geometrical data.

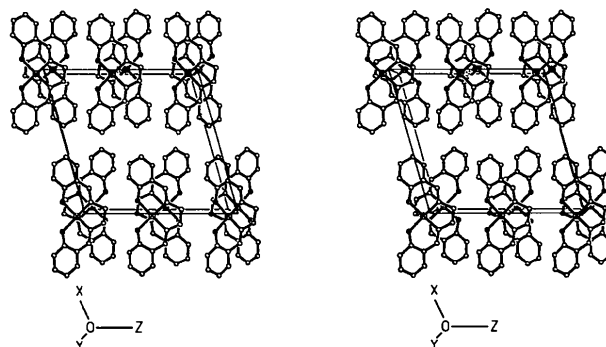


Fig. 2. Stereoscopic view of the crystal structure of Pt–salen down the *y* axis.

Experimental

Pt–salen was prepared by stirring a mixture of Pt(en)Cl₂ (0.5 g) and the Tl salt of salicylaldehyde (1 g) in absolute *N,N'*-dimethylformamide (70 ml) for 20 d at 333 K. Vine-red