

to the nearest Na atoms. The largest residuals in the final difference Fourier map were 1.27 e Å⁻³ at 1.01 Å from O21 and -0.97 e Å⁻³ at 1.21 Å from Y1. For comparison, the electron densities obtained during the structure determination were 6.64 e Å⁻³ for OW8 and 0.66 e Å⁻³ for H82. The isotropic displacement parameters of the H atoms were fixed equal to twice the U_{eq} value of their parent O atom.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1049). Services for accessing these data are described at the back of the journal.

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1,1'-Diacetylferrocene bis(thiosemicarbazone) monohydrate

WEN XIAO,^a ZHONG-LIN LU,^a RUI-YING LI,^a
CHENG-YONG SU,^a BEI-SHENG KANG,^a S. SHANMUGA
SUNDARA RAJ^b AND HOONG-KUN FUN^b

^a*Institute of Physical Chemistry, School of Chemistry & Chemical Engineering, Zhongshan University, Guangzhou 510275, People's Republic of China, and* ^b*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

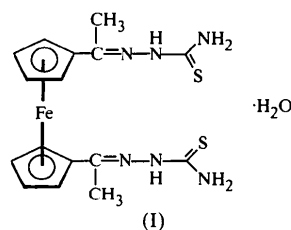
(Received 12 April 1999; accepted 29 June 1999)

Abstract

X-ray analysis reveals that both thiosemicarbazone groups of the title compound, [Fe(C₈H₁₀N₃S)₂·H₂O], are in the keto tautomeric form and that the configuration of the azomethine C=N double bond is *E*. The two cyclopentadienyl rings are parallel and nearly eclipsed. The crystal structure is stabilized by extensive intra- and intermolecular hydrogen bonding involving the water molecule and the thiosemicarbazone moieties.

Comment

Ferrocene and its derivatives have aroused much interest recently as redox-active entities, with potential applications in areas such as materials for molecular electronics (Houlton *et al.*, 1992) and as biologically active compounds (Neuse *et al.*, 1988). In these contexts, considerable interest has been shown in the thio-Schiff base compounds containing a ferrocenyl group, which can coordinate readily with transition metals to give stable complexes (Garg & Kapur, 1990; Ismail, 1997) and which might exhibit large non-linear optical efficiency (Tian *et al.*, 1998). As part of our work on exploring functional coordination complexes for non-linear optical materials, we report here the crystal structure of 1,1'-diacetylferrocene bis(thiosemicarbazone) monohydrate, (I).



The bond lengths in the two thiosemicarbazone groups show slight differences and the C=N, N—N, N—C_{sp²} and C=S bond distances are similar to

values reported in the literature (Fun *et al.*, 1995; Tian *et al.*, 1996), which shows that the molecule is in the keto tautomeric form. The configuration of the C=N bond is *trans*. The Fe—C_{ring} distances are as expected for a ferrocene derivative, ranging from 2.037 (2) to 2.064 (2) Å, with an average of 2.051 (7) Å, which agrees with the values found in diacetylferrocene (2.046 Å; Palenik, 1970) and ferrocene (2.058 Å; Haaland & Sikson, 1968). The dimensions of the cyclopentadienyl (Cp) rings [C—C distances 1.413 (3)–1.441 (2) Å, average 1.426 (9) Å, and C—C—C angles 106.5 (2)–108.6 (2)°, average 108.0 (6)°] are also normal.

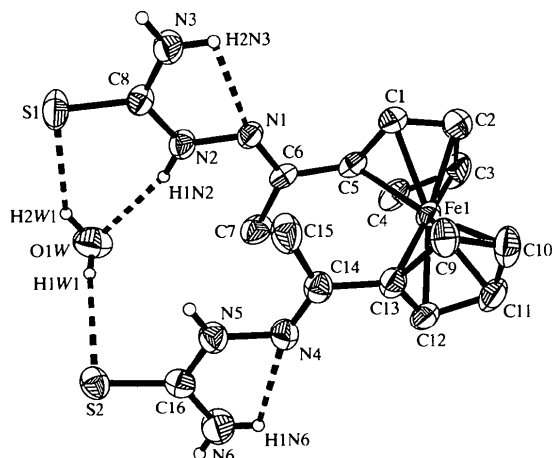


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms bonded to C have been omitted for clarity; other H atoms are shown as spheres of arbitrary size.

The conformation of the Cp rings is close to eclipsed, which is common for ferrocene derivatives. The angle of twist of the Cp rings was defined as the torsion angle between a ring C atom, the two ring centres and the corresponding C atom on the opposite ring (Palenik, 1970). In (I), the average value of this angle of twist is 9.5°. This is probably the result of the intramolecular hydrogen bond. Examples of both staggered and eclipsed conformations are given by Osborne *et al.* (1996) and Houlton *et al.* (1990).

The two Cp rings are planar and nearly parallel, the ring-tilt between the two rings being 3.9 (1)°. The two thiosemicarbazone groups are also planar and are inclined at 7.5 (1)° to each other. The dihedral angles between the Cp1 (C1—C5) and Cp2 (C9—C13) rings and the respective thiosemicarbazone groups are 10.4 (1) and 17.8 (1)°, respectively.

In the crystal lattice, the hydrazone molecules are stacked in planes. The crystal structure is stabilized by a variety of O—H...S, N—H...O and N—H...S hydrogen bonds (Table 2). The water molecule is involved in extensive intra- and intermolecular hydrogen bonds, acting not only as a donor but also as an acceptor.

Experimental

The title compound was synthesized by the reaction of diacetylferrocene and thiosemicarbazide in a 1:2 ratio in ethanol under reflux for 3 h. Single crystals of (I) were obtained by slow evaporation of an ethanol solution at room temperature.

Crystal data

[Fe(C₈H₁₀N₃S)₂].H₂O
M_r = 434.37
 Monoclinic
*C*2/*c*
a = 29.0676 (2) Å
b = 8.8013 (1) Å
c = 18.4470 (1) Å
 β = 125.978 (1)°
V = 3819.09 (5) Å³
Z = 8
D_x = 1.511 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 8192 reflections
 θ = 2.73–33.19°
 μ = 1.027 mm⁻¹
T = 293 (2) K
 Hexagonal
 0.58 × 0.40 × 0.06 mm
 Red

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scan
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 T_{\min} = 0.587, T_{\max} = 0.941
 16 834 measured reflections
 7072 independent reflections

5528 reflections with $I > 2\sigma(I)$
 R_{int} = 0.023
 θ_{\max} = 33.15°
 h = -44 → 41
 k = -8 → 13
 l = -27 → 28
 Intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.038
 $wR(F^2)$ = 0.092
 S = 1.080
 7072 reflections
 323 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0290P)^2 + 3.2041P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
 $\Delta\rho_{\max}$ = 0.388 e Å⁻³
 $\Delta\rho_{\min}$ = -0.563 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C8	1.687 (2)	N3—C8	1.318 (2)
S2—C16	1.699 (2)	N4—C14	1.286 (2)
N1—C6	1.292 (2)	N4—N5	1.388 (2)
N1—N2	1.382 (2)	N5—C16	1.348 (2)
N2—C8	1.354 (2)	N6—C16	1.330 (2)
N1—C6—C5	116.2 (1)	N4—C14—C13	116.42 (14)
N1—C6—C7	124.7 (2)	N4—C14—C15	125.36 (15)
N3—C8—N2	117.6 (2)	N6—C16—N5	116.7 (2)
N3—C8—S1	121.8 (1)	N6—C16—S2	122.7 (1)
N2—C8—S1	120.6 (1)	N5—C16—S2	120.7 (1)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1W1...S2	0.82 (3)	2.50 (3)	3.311 (2)	169 (4)
N2—H1N2...O1W	0.92 (3)	2.15 (2)	3.013 (2)	157 (3)
N6—H1N6...N4	0.81 (3)	2.27 (3)	2.604 (3)	105 (2)
O1W—H2W1...S1	0.88 (5)	2.53 (4)	3.272 (2)	143 (3)

N3—H2N3...N1	0.88 (3)	2.29 (3)	2.656 (3)	105 (2)
N3—H1N3...S2 ¹	0.88 (3)	2.64 (3)	3.512 (2)	175 (2)
N5—H1N5...S1 ¹	0.82 (3)	2.86 (3)	3.656 (2)	163 (2)
N3—H3N3...N1 ⁱⁱ	0.88 (3)	2.43 (2)	3.128 (2)	137 (2)
N6—H2N6...O1W ⁱⁱⁱ	0.81 (3)	2.35 (3)	2.962 (3)	133 (3)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-x, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

All H atoms were refined isotropically; the C—H distances are in the range 0.84 (5)–1.00 (3) Å.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1259). Services for accessing these data are described at the back of the journal.

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Di- μ -azido-bis{[2-(2-aminoethyl)pyridine-*N,N'*]aquacopper(II)} diperchlorate

IBRAHIM ABDUL RAZAK,^a HOONG-KUN FUN,^a KANDASAMY CHINNAKALI,^{a†} S. SHANMUGA SUNDARA RAJ,^a JIA-CHENG LIU^b AND XIAO-ZENG YOU^b

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and

^bCoordination Chemistry Institute & State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China. E-mail: hkfun@usm.my

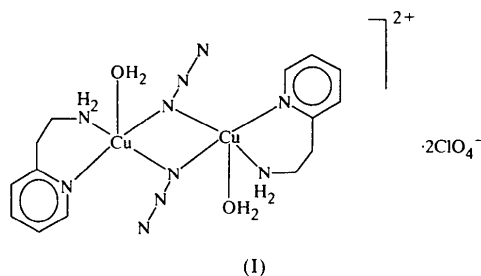
(Received 22 June 1999; accepted 30 June 1999)

Abstract

In the title compound, [Cu₂(N₃)₂(C₇H₁₀N₂)₂(H₂O)₂](ClO₄)₂, the Cu atom is in a distorted square-pyramidal environment with the basal positions occupied by four N atoms, two from a bidentate 2-(2-aminoethyl)pyridine ligand and another two from a centrosymmetrically related azide bridge. The water molecule occupies the axial position. In the crystal, the molecules are in a stacked arrangement and form layers connected by hydrogen bonds involving water molecules and perchlorate ions.

Comment

Copper(II) complexes bridged by azide ligands are of interest because of their bonding mode and magnetic interactions, and also because they exhibit a rich variety of stereochemistries (Kahn, 1993; Hathaway, 1981, 1982). In this paper, we report the synthesis and structure of di- μ -azido-bis{[2-(2-aminoethyl)pyridine-*N,N'*]aquacopper(II)} diperchlorate, (I).



The asymmetric unit consists of one half of the [Cu(C₇H₁₀N₂)(H₂O)(N₃)₂]²⁺ cation and a perchlorate anion. The other half of the cation is generated by a crystallographic inversion centre. The coordination around the Cu atom is a distorted square pyramid, with

† On leave from: Department of Physics, Anna University, Chennai 600 025, India.