

[1,1'-Diferrocenyl-3,3'-(ethane-1,2-diyl)dinitrilo]-dibutanolato]nickel(II) dichloromethane solvate**Peter D.W. Boyd,* Paul M. Johns and Clifton E.F. Rickard**

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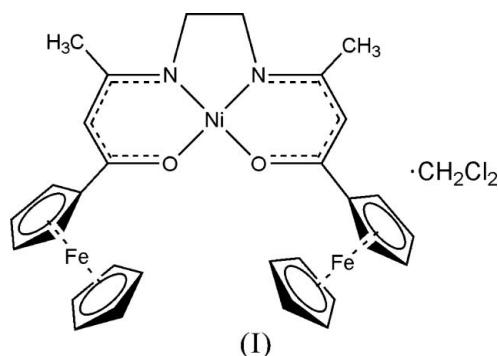
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Key indicatorsSingle-crystal X-ray study
 $T = 200\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.027
 wR factor = 0.070
Data-to-parameter ratio = 15.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Fe}_2\text{Ni}(\text{C}_5\text{H}_5)_2(\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2)]\cdot\text{CH}_2\text{Cl}_2$, is a four-coordinate square-planar nickel(II) complex with a tetradentate 1,1'-diferrocenyl-3,3'-(ethane-1,2-diyl)dinitrilo)dibutanolate ligand, which crystallizes with a molecule of dichloromethane. The ferrocene substituents are arranged in a *syn* conformation with respect to the Ni coordination plane. The complexes stack in an alternating assembly with channels occupied by the solvent molecules.

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The tetradentate ligand formed by the reaction of 1,3-(1-ferrocenyl)butanedione and 1,2-diaminoethane, 1,1'-diferrocenyl-3,3'-(ethane-1,2-diyl)dinitrilo)dibutanol (H_2L), has been shown to form complexes with transition metals and lanthanides (Ma *et al.*, 1991; Zhu *et al.*, 1993; Shi *et al.*, 2004). The X-ray crystal structures of the copper(II) and nickel(II) complexes formed by the reaction of H_2L with the appropriate metal acetate have been determined (Zhu *et al.*, 1993; Shi *et al.*, 2004). In this work, the nickel complex, NiL , has been prepared directly from a template reaction of 1,3-(1-ferrocenyl)butanedione, 1,2-diaminoethane and nickel acetate in methanol. Single crystals of the title dichloromethane solvate, $\text{NiL}\cdot\text{CH}_2\text{Cl}_2$, (I), were grown from cooled dichloromethane solutions of the complex, in contrast with solvent-free crystals grown from a CH_2Cl_2 -ethanol solution (Shi *et al.*, 2004).



The molecular structure of (I) is shown in Fig. 1. The four-coordinate Ni^{II} ion has a near square-planar NiO_2N_2 geometry with similar Ni—N and Ni—O bond lengths (Table 1). The bond lengths and angles are very similar to those in the structure of the unsolvated complex (Shi *et al.*, 2004) and related complexes (Cariati *et al.*, 1976; Lin *et al.*, 1990; Haider *et al.*, 1982; Gupta *et al.* 2002; Malatesta & Mugnoli, 1981; Romanenko *et al.*, 1989; Liu *et al.*, 1989). The Schiff base coordination of Ni is planar; the mean plane through atoms C1—C8/O1/O2/N1/N2/Ni has an r.m.s. deviation of 0.032 Å.

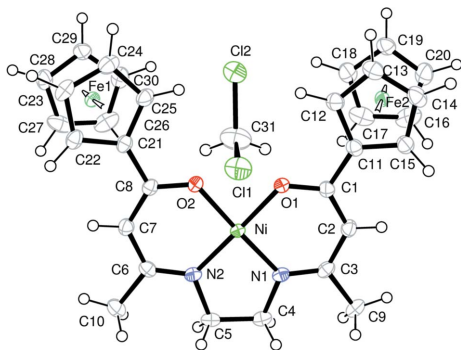


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are shown as arbitrary spheres.

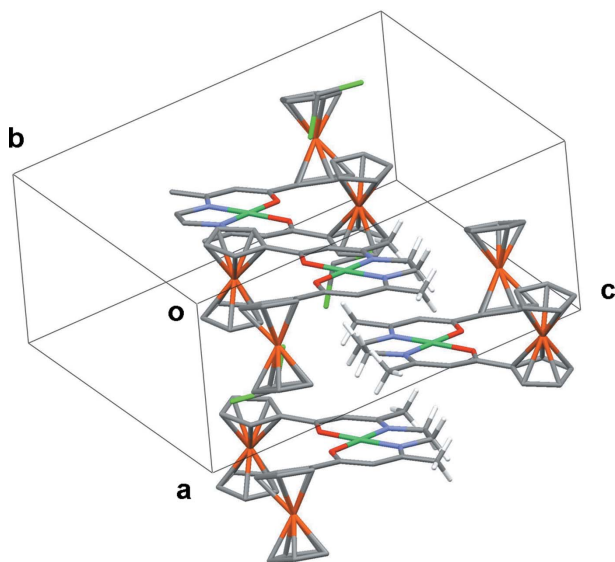


Figure 2
The arrangement of complex (I) in the crystal structure, showing the stacking of columns.

The two ferrocene groups are *syn* with respect to the Schiff base complex, with the ferrocene cyclopentadienyl rings (C11–C15, r.m.s. deviation 0.0024 Å, and C21–C25, r.m.s. deviation 0.0037 Å) making angles of 11.69 (4) and 15.90 (4)°, respectively, with this plane. The cyclopentadienyl rings are in nearly eclipsed arrangements within each ferrocene group. Pseudotorsion angles for C...Cg1...Cg2...C range from 4.90 to 5.79° and those for C...Cg3...Cg4...C range from 7.12 to 7.58° (Cg1 and Cg2 are the centroids of the C11–C15 and C16–C20 rings, respectively, and Cg3 and Cg4 are the centroids of the C21–C25 and C26–C30 rings, respectively). The Fe1...Cg3 and Fe1...Cg4 distances are 1.652 (1) and 1.654 (1) Å, respectively, with a Cg3...Fe...Cg4 angle of 178.34 (6)°. The Fe2...Cg1 and Fe2...Cg2 distances are 1.647 (1) and 1.651 (1) Å, respectively, with a Cg1...Fe...Cg2 angle of 178.46 (6)°.

The molecules in the crystal structure of (I) stack in columns of planar Schiff base complexes, arranged in an alternating assembly along the *a* axis (Fig. 2). There are C–H... π interactions between methyl and methylene groups and

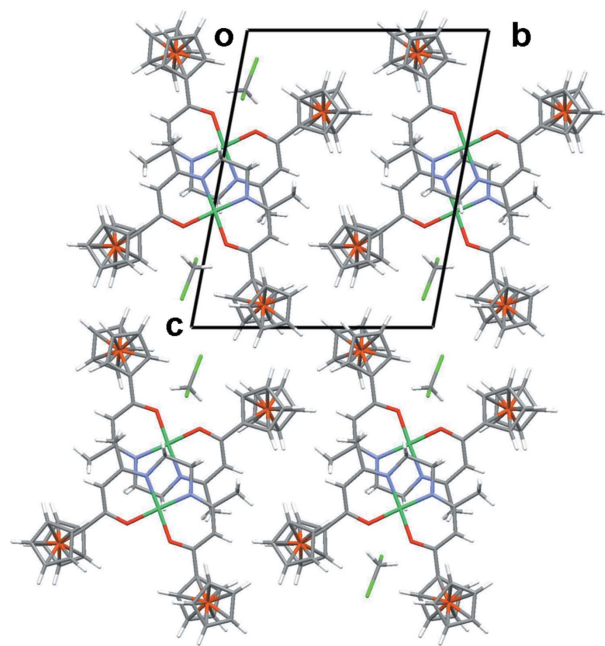


Figure 3
The arrangement of complex (I) in the crystal structure, viewed along the *a* axis, showing channels occupied by dichloromethane solvent molecules.

the six-membered chelate rings of adjacent molecules, with C–H...C(complex) distances ranging from 2.769 to 2.893 Å (Fig. 2). The ferrocene groups also form columns along the *a* axis and this arrangement leads to channels which are occupied by dichloromethane molecules (Fig. 3). There are C–H...O interactions from the dichloromethane to the O atoms of the chelate (C31–H31A...O2 = 2.53 Å and C31–H31B...O1 = 2.54 Å) and longer cyclopentadienyl C–H...Cl contacts [C29–H29...Cl2(–*x*, 2 – *y*, –*z*) = 2.91 Å and C30–H30...Cl2(*x* – 1, *y*, *z*) = 2.90 Å].

Experimental

Complex (I) was prepared by the addition of a warm solution of 1,3-(1-ferrocenyl)butanedione (202 mg, 0.752 mmol) in methanol (20 ml) to a refluxing solution of nickel(II) acetate tetrahydrate (93.5 mg, 0.376 mmol) and 1,2-diaminoethane (25 ml, 0.376 mmol) in methanol (20 ml). The solution was refluxed for 20 h. After cooling, the solution was filtered, and the solid washed with methanol and dried to give the red–brown complex (152 mg 0.245 mmol, 65% yield). Brown crystals of (I) were grown from a refrigerated dichloromethane solution.

Crystal data

[Fe₂Ni(C₅H₅)₂(C₂₀H₂₀N₂O₂)]·
CH₂Cl₂
M_r = 705.90
Triclinic, P $\bar{1}$
a = 7.0218 (1) Å
b = 12.9673 (3) Å
c = 16.3207 (3) Å
 α = 98.143 (1)°
 β = 101.884 (1)°

γ = 100.312 (1)°
V = 1405.91 (5) Å³
Z = 2
D_x = 1.667 Mg m^{–3}
Mo K α radiation
 μ = 1.90 mm^{–1}
T = 200 (2) K
Irregular fragment, brown
0.15 × 0.15 × 0.15 mm

Data collection

Siemens SMART area-detector diffractometer	13215 measured reflections
ω scans	5711 independent reflections
Absorption correction: empirical (using intensity measurements) (<i>XABS2</i> ; Parkin <i>et al.</i> , 1995)	4934 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.729$, $T_{\max} = 0.752$	$R_{\text{int}} = 0.020$
	$\theta_{\max} = 26.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 1.8447P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 0.90$	$\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$
5711 reflections	$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$
363 parameters	
H-atom parameters constrained	

Table 1

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

Ni—O2	1.8496 (15)	Ni—N2	1.8529 (18)
Ni—N1	1.8515 (18)	Ni—O1	1.8575 (15)
O2—Ni—N1	177.85 (8)	O2—Ni—O1	83.18 (7)
O2—Ni—N2	94.93 (7)	N1—Ni—O1	94.75 (8)
N1—Ni—N2	87.16 (8)	N2—Ni—O1	177.23 (8)

H atoms were placed in calculated positions and refined using a riding model, [with C—H = 0.93–1.00 \AA , and with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.2$ for aromatic and methylene H or 1.5 for methyl H. Methyl groups were rotated to fit the H-atom positions to the observed electron density.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *MERCURY* Macrae *et al.*, 2006).

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