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Note

Studies on intramolecular hydrogen bonding of 1,1′-bis[*N*-formyl-*N*′-*p*-chlorophenylthiourea]ferrocene

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Abstract

1,1′-Bis[*N*-formyl-*N*′-*p*-chlorophenylthiourea]ferrocene was synthesized through the reaction of 1,1′-bis[formyl isothiocyanate]ferrocene with *p*-chloroaniline. Its ^{1}H NMR, IR and mass spectra were studied. A single crystal structure determination showed that there are two intramolecular hydrogen bonds between the carbonyl group and N′–H of each N′H–C(S)–NH–C(O) moiety. They form two parallel planar six-membered rings. In addition, the hydrogen bonding rings are basically in the same plane with the Cp rings to which they are attached. This highlights its property in molecular recognition.

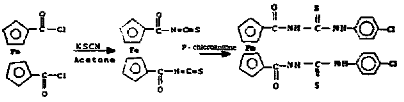
Keywords: Ferrocene complexes; Acyl thiourea complexes; Hydrogen bonding; Crystal structures

1. Introduction

For several years, we have been engaged in the synthesis and coordination chemistry of ferrocenyl-containing acyl thiourea derivatives [1,2]. The existence of intramolecular hydrogen bonds is another interesting problem to be investigated. The introduction of a ferrocene fragment into the molecule often leads to its better crystallizability. The crystal and molecular structure of some mono-substituted ferrocenoyl thioureas have been determined and discussed [3,4]. X-ray diffraction analysis revealed that they contain intramolecular hydrogen bonds. 1,1′-Disubstituted ferrocene derivatives are not only novel polychelate ligands ready to complex with transition metal ions, but also promising host compounds for them in molecular recognition [5]. A series of 1,1′-disubstituted ferrocenoyl thioureas was prepared by treating the product from the reaction of 1,1′-bisferrocenoyl chloride and potassium isothiocyanate with various amines [6]. Among these compounds, the crystal structure of the title compound determined by the X-ray method is reported here. The results of the X-ray analysis reveal that two parallel intramolecular hydrogen bonding rings coexist in one molecule. The title compound reacts with transition metal salts and results in the formation of coordination polymers [6].

2. Experimental

The general experimental techniques and physical measurements were as described before [3]. Mass spectra were recorded on a ZAB-HS mass spectrometer. The following equation shows the preparation of the title compound.



2.1. Synthesis of 1,1′-bis(formyl isothiocyanate)ferrocene

0.533 g (5.5 mmol) KSCN was dissolved in 15 ml acetone and added dropwise to the 20 ml acetone solution of 2.5 mmol $Fc(COCl)_2$ and refluxed for 30 min. The red acetone solution of $Fc(CONCS)_2$ was obtained on filtration of KCl and used in situ for the following reaction without further separation.

2.2. Synthesis of 1,1′-bis[N-formyl-N′-p-chlorophenyl thiourea]ferrocene

0.65 g (5 mmol) *p*-chloroaniline dissolved in 20 ml acetone was added dropwise to the acetone solution of 2.5 mmol

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Fe(CONCS)$_2$. Red solid appeared quickly. The mixture was refluxed for 2 h. Red powders were obtained on filtration and were washed with acetone. A total of 1.39 g was collected. The product is red, yield 91%, melting point 195–197°C, and was recrystallized from acetone/petroleum ether (90–120°C) solution. *Anal.* Found: C, 51.30; H, 3.40; N, 8.93. Calc. for $C_{26}H_{20}Cl_2FeN_4O_2S_2$: C, 51.08; H, 3.30; N, 9.16%. IR data (cm^{-1}): ν(N–H) 3303.9 (m), ν(N′–H) 3200–3015 (w), ν(C=O) 1663.3 (s), ν(C=S) 1326.9 (m), δ(CNH) 1523.8 (vs), ν(C(O)–N) 1269.5 (m), ν(C(S)–N) 1154.7 (vs). ^{1}H NMR (d, ppm): 4.72 (s, 4H, C_5H_4), 4.96 (s, 4H, C_5H_4), 8.84 (s, 2H, N–H), 12.55 (s, 2H, N′–H), 7.32–7.80 (m, 8H, $2C_6H_4$). MS (*m*/*z*): 65, 93, 127 (b), 169, 256, 492.

2.3. X-ray crystallography

Crystals suitable for X-ray examination were obtained by the slow evaporation of an acetone/petroleum ether solution. A single crystal with dimensions of about 0.2 × 0.3 × 0.3 mm was mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromatic Mo Kα radiation (λ = 0.071073 nm). A total of 3240 independent reflections was collected within $4.0 < \theta < 46.0°$ of 2θ–θ scan, at room temperature (299 ± 1 K), among which 1690 were accepted as observable ($I \geq 3\sigma(I)$). The intensities were fully corrected for Lp factors and empirical absorption [7]. The crystal belongs to the monoclinic space group $P2_1/n$, a = 8.435(1), b = 23.088(8), c = 13.307(3) Å, β = 95.70(1)°, V = 2597(2) Å^3, Z = 4, D_c = 1.575 g cm^{-3}, μ = 9.804 cm^{-1} and $F(000)$ = 1248. The crystal structure was solved by the direct phase determination method (MULTAN82). One independent Fe atom was located on an *E*-map. The other non-hydrogen atoms were found in the successive difference Fourier syntheses. The hydrogen atoms were not included in the refinement and the calculations of structure factors. The coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares method and converged to R = 0.053 and R_w = 0.061 with unit weights. The highest electron density on the final difference Fourier map was found to be 0.45 e Å^{-3}. All calculations were performed on a PDP11/44 computer using the SDP-PLUS program system.

3. Results and discussion

3.1. Infrared investigation

A strong absorption at 1663.3 cm^{-1} is attributed to the stretching vibrations of the carbonyl groups attached to ferrocenyl. Not only the conjugate resonance with Cp rings is responsible for its decreased wavenumber, but the formation of an intramolecular hydrogen bond with N′–H as well. A very strong band at 1523.8 cm^{-1} is ascribed to δ(CNH). The ν(N–C=O) band is observed at 1269.5 cm^{-1}. It is weaker than either ν(C=O) or δ(CNH), presumably due to a mixed vibration involving –N–C=O and N–H modes [8], which also supports the hypothesis of the presence of the intramolecular hydrogen bond. The medium intensity band at 3303.9 cm^{-1} is assigned as the stretching vibration frequency of the NH group attached to carbonyl. The broad and weak band in the region 3200–3015 cm^{-1} is classified to be the stretching vibration of N′–H. The medium band at 1326.9 cm^{-1} is supposed to be ν(C=S) as reported before [3,4], and the strong band at 1154.7 cm^{-1} is the ν(C(S)–N) vibration.

3.2. ^{1}H NMR investigation

The protons on the substituted Cp rings give rise to an AA′BB′ type resonance. N′H gives δ 12.55 ppm at lower

Table 1
Fractional coordinates and equivalent isotrpic thermal parameters of non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Fe	0.2817(2)	0.15959(7)	0.8659(1)	3.47(3)
Cl(1)	−0.5838(4)	−0.1384(1)	0.4764(3)	5.11(8)
Cl(2)	−0.2534(5)	−0.2526(1)	0.4584(3)	6.63(9)
S(1)	−0.2198(4)	−0.0207(2)	0.9223(3)	4.97(8)
S(2)	0.1715(4)	−0.1158(1)	0.8670(3)	4.57(8)
O(1)	−0.1262(9)	0.1379(4)	0.7362(6)	4.8(2)
O(2)	0.1440(9)	0.0433(3)	0.6708(5)	4.4(2)
N(1)	−0.257(1)	0.0368(4)	0.7469(6)	3.4(2)
N(2)	−0.112(1)	0.0810(4)	0.8794(7)	3.5(2)
N(3)	0.052(1)	−0.0612(4)	0.6978(6)	3.1(2)
N(4)	0.198(1)	−0.0077(4)	0.8200(6)	3.2(2)
C(11)	−0.485(1)	−0.0887(5)	0.5585(9)	3.6(3)
C(12)	−0.373(1)	−0.0532(5)	0.5229(8)	3.2(3)
C(13)	−0.295(1)	−0.0120(5)	0.5884(8)	3.5(3)
C(14)	−0.339(1)	−0.0080(5)	0.6878(8)	3.2(3)
C(15)	−0.455(1)	−0.0443(5)	0.7231(9)	3.7(3)
C(16)	−0.528(1)	−0.0849(5)	0.6565(8)	3.7(3)
C(17)	−0.201(1)	0.0353(5)	0.8431(9)	3.6(3)
C(18)	−0.070(1)	0.1293(5)	0.8237(9)	3.9(3)
C(21)	0.046(1)	0.1698(5)	0.8770(9)	3.9(3)
C(22)	0.103(1)	0.2187(5)	0.8247(9)	4.2(3)
C(23)	0.226(1)	0.2454(5)	0.893(1)	5.1(3)
C(24)	0.244(2)	0.2115(5)	0.9871(9)	4.9(3)
C(25)	0.128(1)	0.1634(5)	0.9768(8)	3.9(3)
C(31)	−0.156(1)	−0.1983(5)	0.5320(9)	4.3(3)
C(32)	−0.190(1)	−0.1920(5)	0.6329(9)	4.5(3)
C(33)	−0.118(1)	−0.1478(5)	0.6915(9)	4.3(3)
C(34)	−0.015(1)	−0.1118(4)	0.6460(9)	3.5(3)
C(35)	0.017(1)	−0.1177(5)	0.5465(8)	3.5(3)
C(36)	−0.055(1)	−0.1613(5)	0.4875(9)	4.0(3)
C(37)	0.134(1)	−0.0601(4)	0.7899(8)	3.1(2)
C(38)	0.214(1)	0.0401(5)	0.7559(8)	3.7(3)
C(41)	0.329(1)	0.0852(5)	0.7944(8)	3.1(3)
C(42)	0.369(1)	0.1336(5)	0.7335(9)	3.9(3)
C(43)	0.486(1)	0.1674(5)	0.7930(9)	4.5(3)
C(44)	0.519(1)	0.1382(5)	0.887(1)	4.8(3)
C(45)	0.424(1)	0.0876(5)	0.8919(9)	3.6(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent parameter defined as: $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 2
Selected bond distances Å and angles (°) between non-hydrogen atoms

	Fe	C(21)	2.025(6)		C(11)	C(12)	1.367(8)
	Fe	C(22)	2.065(7)		C(11)	C(16)	1.394(9)
	Fe	C(23)	2.078(8)		C(12)	C(13)	1.409(9)
	Fe	C(24)	2.059(6)		C(13)	C(14)	1.412(9)
	Fe	C(25)	2.060(7)		C(14)	C(15)	1.406(8)
	Fe	C(41)	2.022(6)		C(15)	C(16)	1.392(9)
	Fe	C(42)	2.065(6)		C(18)	C(21)	1.48(1)
	Fe	C(43)	2.065(7)		C(21)	C(22)	1.43(1)
	Fe	C(44)	2.056(7)		C(21)	C(25)	1.443(9)
	Fe	C(45)	2.060(6)		C(22)	C(23)	1.45(2)
	Cl(1)	C(11)	1.740(7)		C(23)	C(24)	1.47(1)
	Cl(2)	C(31)	1.743(7)		C(24)	C(25)	1.49(1)
	S(1)	C(17)	1.685(7)		C(31)	C(32)	1.41(1)
	S(2)	C(37)	1.657(6)		C(31)	C(36)	1.38(1)
	O(1)	C(18)	1.227(8)		C(32)	C(33)	1.39(1)
	O(2)	C(38)	1.226(7)		C(33)	C(34)	1.38(1)
	N(1)	C(14)	1.434(9)		C(34)	C(35)	1.384(9)
	N(1)	C(17)	1.321(8)		C(35)	C(36)	1.381(9)
	N(2)	C(17)	1.356(9)		C(38)	C(41)	1.478(9)
	N(2)	C(18)	1.403(8)		C(41)	C(42)	1.440(8)
	N(3)	C(34)	1.443(8)		C(41)	C(45)	1.460(9)
	N(3)	C(37)	1.347(8)		C(42)	C(43)	1.432(9)
	N(4)	C(37)	1.365(8)		C(43)	C(44)	1.43(1)
	N(4)	C(38)	1.410(8)		C(44)	C(45)	1.421(9)
C(21)	Fe	C(22)	41.0(3)	C(24)	Fe	C(41)	156.3(3)
C(21)	Fe	C(23)	68.5(3)	C(24)	Fe	C(42)	158.9(3)
C(21)	Fe	C(24)	69.4(4)	C(24)	Fe	C(43)	121.1(3)
C(21)	Fe	C(25)	41.4(2)	C(24)	Fe	C(44)	104.7(3)
C(21)	Fe	C(41)	111.9(3)	C(24)	Fe	C(45)	118.0(4)
C(21)	Fe	C(42)	122.2(3)	C(25)	Fe	C(41)	122.6(3)
C(21)	Fe	C(43)	153.6(3)	C(25)	Fe	C(42)	157.8(3)
C(21)	Fe	C(44)	166.0(4)	C(25)	Fe	C(43)	161.1(3)
C(21)	Fe	C(45)	130.1(3)	C(25)	Fe	C(44)	125.9(3)
C(22)	Fe	C(23)	40.9(3)	C(25)	Fe	C(45)	108.2(3)
C(22)	Fe	C(24)	70.1(4)	C(41)	Fe	C(42)	41.3(2)
C(22)	Fe	C(25)	70.6(3)	C(41)	Fe	C(43)	69.0(3)
C(22)	Fe	C(41)	127.4(3)	C(41)	Fe	C(44)	68.2(3)
C(22)	Fe	C(42)	106.1(3)	C(41)	Fe	C(45)	42.0(2)
C(22)	Fe	C(43)	115.9(3)	C(42)	Fe	C(43)	40.6(2)
C(22)	Fe	C(44)	150.5(3)	C(42)	Fe	C(44)	67.8(3)
C(22)	Fe	C(45)	167.3(3)	C(42)	Fe	C(45)	69.9(3)
C(23)	Fe	C(24)	41.6(3)	C(43)	Fe	C(44)	40.5(3)
C(23)	Fe	C(25)	70.3(3)	C(43)	Fe	C(45)	69.5(3)
C(23)	Fe	C(41)	162.1(3)	C(44)	Fe	C(45)	40.5(3)
C(23)	Fe	C(42)	122.4(3)	C(14)	N(1)	C(17)	128.2(6)
C(23)	Fe	C(43)	102.4(3)	C(17)	N(2)	C(18)	126.2(6)
C(23)	Fe	C(44)	116.1(3)	C(34)	N(3)	C(37)	126.4(5)
C(23)	Fe	C(45)	151.6(3)	C(37)	N(4)	C(38)	125.2(6)
C(24)	Fe	C(25)	42.1(4)	Cl(1)	C(11)	C(12)	118.9(6)
Cl(1)	C(11)	C(16)	118.2(6)	Fe	C(23)	C(24)	68.6(4)
C(12)	C(11)	C(16)	122.8(6)	C(22)	C(23)	C(24)	108.6(6)
C(11)	C(12)	C(13)	119.1(7)	Fe	C(24)	C(23)	69.9(4)
C(12)	C(13)	C(14)	118.3(6)	Fe	C(24)	C(25)	69.0(4)
N(1)	C(14)	C(13)	113.9(5)	C(23)	C(24)	C(25)	107.9(6)
N(1)	C(14)	C(15)	124.0(7)	Fe	C(25)	C(21)	68.1(4)
C(13)	C(14)	C(15)	122.1(7)	Fe	C(25)	C(24)	68.9(4)
C(14)	C(15)	C(16)	118.0(6)	C(21)	C(25)	C(24)	105.2(6)
C(11)	C(16)	C(15)	119.7(6)	Cl(2)	C(31)	C(32)	118.8(5)
S(1)	C(17)	N(1)	125.4(5)	Cl(2)	C(31)	C(36)	118.6(6)
S(1)	C(17)	N(2)	117.3(5)	C(32)	C(31)	C(36)	122.6(6)
N(1)	C(17)	N(2)	117.2(6)	C(31)	C(32)	C(33)	119.4(7)

(*continued*)

Table 2 (*continued*)

O(1)	C(18)	N(2)	122.6(6)	C(32)	C(33)	C(34)	117.1(7)
O(1)	C(18)	C(21)	121.6(7)	N(3)	C(34)	C(33)	120.8(6)
N(2)	C(18)	C(21)	115.9(7)	N(3)	C(34)	C(35)	115.5(6)
Fe	C(21)	C(18)	119.9(5)	C(33)	C(34)	C(35)	123.5(6)
Fe	C(21)	C(22)	71.0(4)	C(34)	C(35)	C(36)	119.9(7)
Fe	C(21)	C(25)	70.6(4)	C(31)	C(36)	C(35)	117.7(6)
C(18)	C(21)	C(22)	120.1(6)	S(2)	C(37)	N(3)	126.6(5)
C(18)	C(21)	C(25)	127.6(6)	S(2)	C(37)	N(4)	117.5(5)
C(22)	C(21)	C(25)	111.9(6)	N(3)	C(37)	N(4)	115.8(5)
Fe	C(22)	C(21)	68.0(4)	O(2)	C(38)	N(4)	122.7(6)
Fe	C(22)	C(23)	70.0(4)	O(2)	C(38)	C(41)	121.1(6)
C(21)	C(22)	C(23)	106.4(6)	N(4)	C(38)	C(41)	116.2(7)
Fe	C(23)	C(22)	69.1(4)	Fe	C(41)	C(38)	127.6(4)
Fe	C(41)	C(42)	71.0(4)	Fe	C(43)	C(44)	69.4(4)
Fe	C(41)	C(45)	70.5(4)	C(42)	C(43)	C(44)	107.1(6)
C(38)	C(41)	C(42)	122.3(6)	Fe	C(44)	C(43)	70.1(5)
C(38)	C(41)	C(45)	128.4(6)	Fe	C(44)	C(45)	70.0(4)
C(42)	C(41)	C(45)	109.2(6)	C(43)	C(44)	C(45)	111.4(6)
Fe	C(42)	C(41)	67.7(4)	Fe	C(45)	C(41)	67.7(3)
Fe	C(42)	C(43)	69.8(4)	Fe	C(45)	C(44)	69.6(4)
C(41)	C(42)	C(43)	107.5(6)	C(41)	C(45)	C(44)	104.9(6)
Fe	C(43)	C(42)	69.7(4)				
Hydrogen bonding							
N(1)···O(1)	2.592(5)	N(3)···O(2)	2.571(5)				
C(17)–N(1)···O(1)	87.9(4)	C(37)–N(3)···O(2)	88.5(4)				
N(1)–O(1)···C(18)	85.8(4)	N(3)–O(2)···C(38)	86.5(4)				

Numbers in parentheses are e.s.d.s in the least significant digits.

field and NH gives δ 8.84 ppm at higher field, which is interpreted to be the result of the deshielding effect of the intramolecular hydrogen bond and the shielding effect of the thione group, respectively. The same phenomena were observed in monoformylthiourea substituted ferrocene derivatives [3,4].

3.3. Mass spectra

Due to its instability toward electron impact, no molecular ion peak is collected. The base peak at 127 is considered to be the $ClC_6H_4NH_2^{\cdot +}$ fragment. The 65 and 93 peaks are ascribable to the $C_5H_5^+$ and $C_5H_5CO^+$ ions, respectively.

Table 3
Least-squares planes

Equation of plane 1: $0.852(2)X-0.447(3)Y-0.271(5)Z+5.77(4)=0$								
Atom	N(1)	C(17)	N(2)	C(18)	O(1)			
Distances to plane (Å)	0.02(1)	−0.01(1)	−0.02(1)	0.04(1)	−0.03(1)			
Equation of plane 2: $-0.680(3)X+0.668(3)Y-0.300(4)Z+0.29(4)=0$								
Atom	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)		
Distances to plane (Å)	−0.00(8)	0.00(9)	0.00(6)	0.00(2)	0.00(1)	0.00(1)		
Equation of plane 3: $0.725(4)X-0.578(4)Y-0.373(5)Z+7.16(6)=0$								
Atom	C(21)	C(22)	C(23)	C(24)	C(25)			
Distances to plane (Å)	−0.00(1)	0.00(1)	−0.00(1)	0.00(6)	−0.00(1)			
Equation of plane 4: $0.874(2)X-0.341(3)Y-0.343(5)Z+3.09(4)=0$								
Atom	N(3)	C(37)	N(4)	C(38)	O(2)			
Distances to plane (Å)	−0.02(1)	0.05(1)	0.06(1)	0.04(1)	0.01(1)			
Equation of plane 5: $-0.739(3)X+0.606(4)Y-0.290(4)Z+3.32(3)=0$								
Atom	C(31)	C(32)	C(33)	C(34)	C(35)	C(36)		
Distances to plane (Å)	0.00(1)	0.00(1)	0.00(1)	0.00(1)	0.00(1)	0.00(1)		
Equation of plane 6: $0.758(4)X-0.536(5)Y-0.370(5)Z+3.63(6)=0$								
Atom	C(41)	C(42)	C(43)	C(44)	C(45)			
Distances to plane (Å)	0.00(1)	0.00(1)	0.01(1)	0.00(1)	0.00(1)			
Planes	1–2	1–3	1–4	1–5	1–6	2–3	2–4	2–5
Dihedral angle (°)	142.87	11.98	7.45	145.35	9.32	140.16	136.10	4.91
Planes	2–6	3–4	3–5	3–6	4–5	4–6	5–6	
Dihedral angle (°)	139.78	16.20	141.14	3.05	138.98	13.15	141.16	

The absorption of the (η^5-C_5H_4($CONH_2$)FeC_5H_4CO fragment appears at 256. The 492 peak is the molecular ion peak of 1,1′-bis[*N*-*p*-chloro-aniline amide], which is the Mclafferty rearrangement product of the title compound, losing two molecules of HNCS.

3.4. *Results of X-ray diffraction analysis*

The fractional coordinates and thermal parameters for non-hydrogen atoms are listed in Table 1, and selected bond distances and angles in Table 2.

X-ray analysis reveals that in each molecule there exist two independent intramolecular hydrogen bonds between the carbonyl oxygen and the hydrogen atom on N′ in each –C(O)–NH–C(S)–N′H– moiety, forming two parallel six-membered rings. The planar rings are approximately in the same plane with the cyclopentadienyl rings to which they are attached. The two phenyl rings are basically parallel as well. The molecular structure of the title compounds is very regular as depicted in Fig. 1 and its packing in a unit cell is illustrated in Fig. 2. Table 3 lists the least-squares planes of relevant groups and the dihedral angles between them, and Table 4 shows selected torsion angles. This crystal consists of discrete molecules and the contact distances between the molecules are normal van der Waals distances.

The sandwich structure of ferrocene causes great differences in the properties of mono- and 1,1′-disubstituted ferrocene derivatives, since the two coplanar cyclopentadienyl rings may rotate with respect to each other about the iron

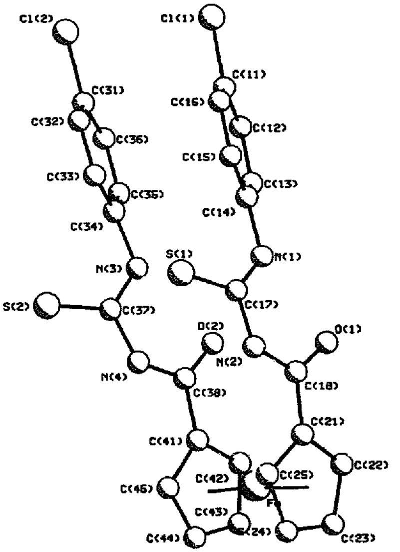

Fig. 1. The molecular structure of the title compound showing the atomic labeling scheme.

Table 4
Selected torsion angles

C(17)	N(1)	C(14)	C(13)	−140(1)	C(17)	N(1)	C(14)	C(15)	41(2)
C(14)	N(1)	C(17)	S(1)	−3(2)	C(14)	N(1)	C(17)	N(2)	172.7(9)
C(18)	N(2)	C(17)	S(1)	174.2(8)	C(18)	N(2)	C(17)	N(1)	−2(1)
C(17)	N(2)	C(18)	O(1)	8(2)	C(17)	N(2)	C(18)	C(21)	−172(1)
C(37)	N(3)	C(34)	C(33)	54(1)	C(37)	N(3)	C(34)	C(35)	−132(1)
C(34)	N(3)	C(37)	S(2)	−2(1)	C(34)	N(3)	C(37)	N(4)	174.9(9)
C(38)	N(4)	C(37)	S(2)	162.9(8)	C(38)	N(4)	C(37)	N(3)	−15(1)
C(37)	N(4)	C(38)	O(2)	15(2)	C(37)	N(4)	C(38)	C(41)	−161(1)
Cl(1)	C(11)	C(12)	C(13)	178.6(8)	C(16)	C(11)	C(12)	C(13)	2(2)
Cl(1)	C(11)	C(16)	C(15)	−178.0(9)	C(12)	C(11)	C(16)	C(15)	−1(2)
C(11)	C(12)	C(13)	C(14)	−2(2)	C(12)	C(13)	C(14)	N(1)	−177.5(9)
C(12)	C(13)	C(14)	C(15)	1(2)	N(1)	C(14)	C(15)	C(16)	177(1)
C(13)	C(14)	C(15)	C(16)	−0.5(1.6)	C(14)	C(15)	C(16)	C(11)	0.6(1.6)
O(1)	C(18)	C(21)	C(22)	−4(2)	O(1)	C(18)	C(21)	C(25)	−176(1)
N(2)	C(18)	C(21)	C(22)	176(1)	N(2)	C(18)	C(21)	C(25)	4(2)
C(18)	C(21)	C(22)	C(23)	−174(1)	C(25)	C(21)	C(22)	C(23)	−1(1)
C(18)	C(21)	C(25)	C(24)	173(1)	C(22)	C(21)	C(25)	C(24)	0(1)
C(21)	C(22)	C(23)	C(24)	1(1)	C(22)	C(23)	C(24)	C(25)	−1(1)
C(23)	C(24)	C(25)	C(21)	1(1)	Cl(2)	C(31)	C(32)	C(33)	−177.9(9)
C(36)	C(31)	C(32)	C(33)	−1(2)	Cl(2)	C(31)	C(36)	C(35)	178.3(8)
C(32)	C(31)	C(36)	C(35)	2(2)	C(31)	C(32)	C(33)	C(34)	0(2)
C(32)	C(33)	C(34)	N(3)	174(1)	C(32)	C(33)	C(34)	C(35)	0(2)
N(3)	C(34)	C(35)	C(36)	−173(1)	C(33)	C(34)	C(35)	C(36)	0(2)
C(34)	C(35)	C(36)	C(31)	−1(2)	O(2)	C(38)	C(41)	C(42)	−3(2)
O(2)	C(38)	C(41)	C(45)	−178(1)	N(4)	C(38)	C(41)	C(42)	173.8(9)
N(4)	C(38)	C(41)	C(45)	−2(2)	C(38)	C(41)	C(42)	C(43)	−178(1)
C(45)	C(41)	C(42)	C(43)	−2(1)	C(38)	C(41)	C(45)	C(44)	177(1)
C(42)	C(41)	C(45)	C(44)	1(1)	C(41)	C(42)	C(43)	C(44)	2(1)
C(42)	C(43)	C(44)	C(45)	−2(1)	C(43)	C(44)	C(45)	C(41)	1(1)

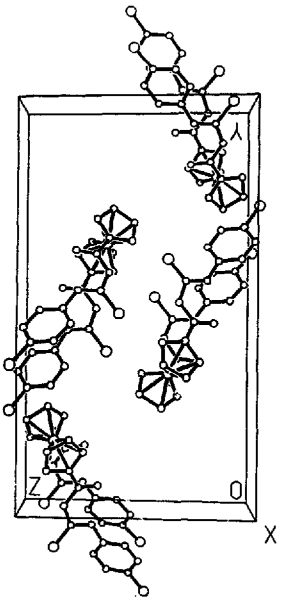

Fig. 2. Unit cell of the title compounds.

center. As long as there are suitable functional groups for the substrate on the substituents in the 1,1'-disubstituted ferrocene system, the side chains can rotate to the optimal spatial arrangement selectively and organize the correct conformation as a receptor, in spite of steric hindrances, thus providing an element for molecular recognition. Constable reviewed Gokel et al.'s works in this field [5]. We explored the coordinate property of the title compounds and found it can act as good host compound for transition metal ions with respect to molecular recognition. Unlike Gokel et al.'s result in which the two substituents rotate to the same side and encircle the guest molecule, the two substituents of the title compound extend to the reverse direction and form coordination polymers with transition metal ions. In addition, the redox potential of the ferrocenyl group is influenced by the guest transition metal ion. The X-ray diffraction spectra of the coordination polymer have been obtained [6].

Acknowledgements

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