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## Synthesis, crystal structure, and properties of a binuclear Zn(II) macroheterocyclic complex based on ferrocene-thiocarbazide ligand

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A binuclear macroheterocyclic complex  $Zn_2(FcL)_2$  based on ferrocene-thiocarbazide (FcL) was synthesized. X-ray diffraction analysis shows that it belongs to the monoclinic system  $P2(1)/n$  space group, with  $a = 1.35379(17)$  nm,  $b = 2.6026(3)$  nm,  $c = 1.8693(2)$  nm,  $\beta = 95.687(2)^\circ$  and final  $R$  indices  $R = 0.0796$  and  $R_w = 0.2119$ . Two Zn(II) ions and two FcL ligands form a 22-membered macroheterocycle, further extended to an infinite 1-D helical chain by intermolecular hydrogen bonding. Spectral properties of the title complex and electrochemical properties of the ligand FcL are also discussed.

**Keywords:** Synthesis; Electrochemical response; Ferrocene macroheterocycle; Helical chain

### 1. Introduction

Design and synthesis of macroheterocyclic metal complexes have seen rapid growth in structural and materials chemistry because of their fascinating architectures and topologies [1] and potential applications in molecular recognition [2–4], catalysis [5], electrochemistry [6, 7], and materials science [8–10]. Rigid aromatic ligands such as ferrocene carboxylic acid [11, 12], 4,4'-biphenyldicarboxylic acid [13, 14], and 2,2'-bipyridyl-4,4'-dicarboxylic acid [15] have been used. Coordination compounds built by metal ions with flexible ferrocene-containing ligands are rare. In contrast to rigid ligands, flexible ones exhibit more conformational and coordination versatility and hence can control and adjust the structure of the resulting coordination frameworks [16]. For example, bifunctional flexible ligands with conformational flexibility can induce a variety of structures leading to supramolecular isomers [17–19]. Ligands containing conjugated S and N atoms could form intriguing structures and exhibit unique properties [20]. A series of coordination frameworks were constructed by using the flexible ligand  $H_2tzda$ , containing carboxyl group, as building blocks [ $H_2tzda = (1,3,4\text{-thiadiazole-2,5-diylidithio})diacetic\ acid$ ] [21]. However, the assembly of macroheterocyclic metal complexes with predicted structures and properties is still

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a challenge for chemists and material scientists. The present research is to design and synthesize a flexible 1,1'-disubstituted ferrocene-containing ligand and use it to prepare such substances. Herein, we report the synthesis, crystal structure, and properties of  $\text{Zn}_2(\text{FcL})_2$ .

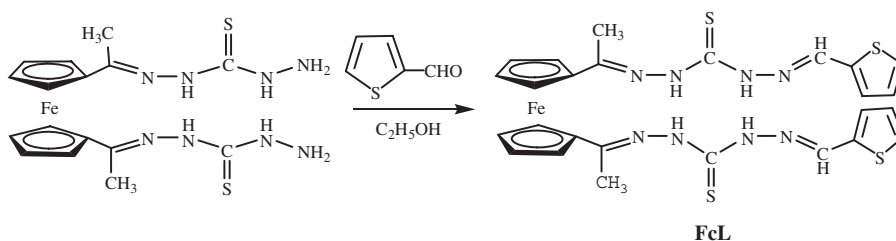
## 2. Experimental

### 2.1. Materials and physical measurements

1,1'-Bis[thiocarbonohydrazone-1-ethylidene] ferrocene was prepared as previously reported [22]. Other reagents were used as received from commercial suppliers without purification. IR spectra of the ligand and complex were measured on a Perkin-Elmer FTIR-1750 spectrometer. Microanalyses were performed on a Flash 1112 EA instrument. The  $^1\text{H}$  NMR spectra of the ligand were recorded at room temperature on a 400 MHz Bruker DPX spectrometer; chemical shifts are denoted in  $\delta$  (ppm) relative to  $\text{Me}_4\text{Si}$  as internal standard. UV-Vis spectra were recorded on a Unico<sup>TM</sup> UV-2102 PC spectrometer. Electrochemical experiments were performed in acetonitrile with a CHI 650A electrochemical analyzer using a conventional three electrode system, a GC working electrode, a Pt gauze counter electrode and an Ag/AgCl reference electrode at ambient temperature.

### 2.2. Synthesis of 1,1'-bis[(2-thiophenylmethylidene)thiocarbonohydrazone-1-ethylidene]ferrocene (FcL)

Ferrocene-thiocarbazide (FcL) was prepared according to scheme 1. 2-Thiophenealdehyde (2.46 g, 22 mmol) was dissolved in 10 mL ethanol and added dropwise to a magnetically stirred solution of 1,1'-bis[thiocarbonohydrazone-1-ethylidene] ferrocene (4.46 g, 10 mmol) in 30 mL ethanol. The mixture was refluxed for 3 h. After cooling, the pink solid FcL formed was filtered, washed with ethanol and dried in air. Yield: 76%. IR(KBr,  $\text{cm}^{-1}$ ): 3448(s), 3115(w), 2964(s), 1592(s), 1520(s), 1250(s), 1112(m), 1041(w), 854(m), 818(m), 766(m), 724(m), 544(w), and 481(m). Anal. Calcd for  $\text{C}_{26}\text{H}_{26}\text{FeN}_8\text{S}_4$  (%): C, 49.20; H, 4.13; N, 17.66; S, 20.21. Found (%): C, 49.38; H, 4.20; N, 17.51; S, 19.86.  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  (ppm): 2.49(s, 3H,  $-\text{CH}_3$ ), 4.45(s, 2H, H-3 H-4,  $-\text{Fc}$ ), 4.80(s, 2H, H-2 H-5,  $-\text{Fc}$ ), 6.92–7.39(m, 3H, thiophene ring), 8.30(s, 1H,  $-\text{CH}=\text{N}$ ), 10.36(s, 1H,  $-\text{NH}$ ); 10.40(s, 1H,  $-\text{NH}$ ); UV-Vis(DMF)  $\lambda_{\text{max}}$ : 335 nm.



Scheme 1. Synthesis route of FcL.

Table 1. Selected bond lengths (Å) and angles (°) for the complex.

C(14)–N(4)	1.2396	N(1)–C(11)	1.327(13)
S(8)–C(52)	1.687(14)	S(5)–C(39)	1.758(11)
N(4)–N(3)	1.4120	N(9)–N(10)	1.355(11)
N(12)–C(40)	1.254(11)	N(15)–C(47)	1.393(11)
Zn(1)–N(1)	2.029(8)	Zn(2)–N(13)	2.056(9)
Zn(1)–S(1)	2.253(3)	Zn(2)–S(3)	2.282(3)
N(1)–Zn(1)–N(12)	110.9(3)	N(8)–Zn(2)–N(13)	116.3(3)
N(8)–Zn(2)–S(7)	123.9(2)	N(12)–Zn(1)–S(5)	86.6(2)
S(7)–Zn(2)–S(3)	126.13(13)	C(22)–N(8)–Zn(2)	127.2(7)
N(2)–N(1)–Zn(1)	115.6(7)	N(11)–N(12)–Zn(1)	116.6(6)
C(13)–S(1)–Zn(1)	91.7(4)	C(45)–N(13)–Zn(2)	127.5(7)
C(11)–N(1)–Zn(1)	127.9(8)	N(13)–C(45)–C(32)	125.4(10)
N(12)–Zn(1)–S(1)	128.8(2)	C(21)–N(7)–N(8)	113.6(8)
S(1)–Zn(1)–S(5)	125.17(12)	N(14)–C(47)–S(7)	132.0(8)

### 2.3. Synthesis of the binuclear complex

A total of  $\text{Zn}(\text{CH}_3\text{COO})_2$  (0.92 g, 5 mmol) in 20 mL ethanol was added dropwise to a magnetically stirred solution of 1,1'-bis[(2-thiophenylmethylidene)thiocarbonylhydrazono-1-ethylidene] ferrocene (3.17 g, 5 mmol) in 50 mL of dimethylformamide (DMF). The mixture was refluxed for 2 h. After cooling, the red solid  $\text{Zn}_2(\text{FcL})_2$  was filtered and washed with ethanol. Red crystals suitable for single-crystal X-ray diffraction were gained after recrystallization in water, ethanol, and DMF with the mole ratio of 1 : 2 : 10. Yield: 38%. IR (KBr,  $\text{cm}^{-1}$ ): 3448(s), 1652(s), 1565(s), 1277(s), 1244(s), 1225(s), 1055(w), 840(m), 823(m), 758(w), 715(m), and 474(w). Anal. Calcd for  $\text{C}_{52}\text{H}_{56}\text{Fe}_2\text{N}_{16}\text{O}_2\text{S}_8\text{Zn}_2$  (%): C, 44.57; H, 3.71; N, 16.01; S, 18.30. Found (%): C, 44.22; H, 3.68; N, 15.85; S, 17.98. UV-Vis(DMF)  $\lambda_{\text{max}}$ : 305 nm.

### 2.4. Structure determination

X-ray single-crystal diffraction data for the complex were collected on a Bruker Smart 1000 CCD diffractometer at 295(2) K with Mo-K $\alpha$  radiation ( $\lambda = 0.071073$  nm) with 12174  $I > 2\theta$  reflections. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [23]; all nonhydrogen atoms were refined anisotropically with the full matrix least squares based on  $F^2$ . Hydrogens were included but not refined. The crystal data and selected parameters are given in tables 1 and 2.

## 3. Results and discussion

### 3.1. Structure description

The crystal structure of the binuclear complex is monoclinic P2(1)/n space group, with  $a = 13.537\ 9(17)$  nm,  $b = 2.6026(3)$  nm,  $c = 1.8693(2)$  nm,  $\beta = 95.687(2)^\circ$ ,  $V = 6.553\ 8(14)$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.451$  Mg m<sup>-3</sup>, crystal size  $0.22 \times 0.19 \times 0.09$  mm<sup>3</sup>,

Table 2. Hydrogen bonds lengths and angles for the complex (Å and °).

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
O(1)–H(2W)...O(2)#1	0.84	1.61	2.21(3)	125.1
N(15)–H(15)...S(1)#2	0.86	2.73	3.454(9)	143.4
N(10)–H(10D)...S(3)	0.86	3.00	3.706(9)	140.7
N(6)–H(6)...S(5)	0.86	2.87	3.598(8)	143.3
N(3)–H(3D)...O(1)#3	0.87	2.15	3.014(19)	172.2

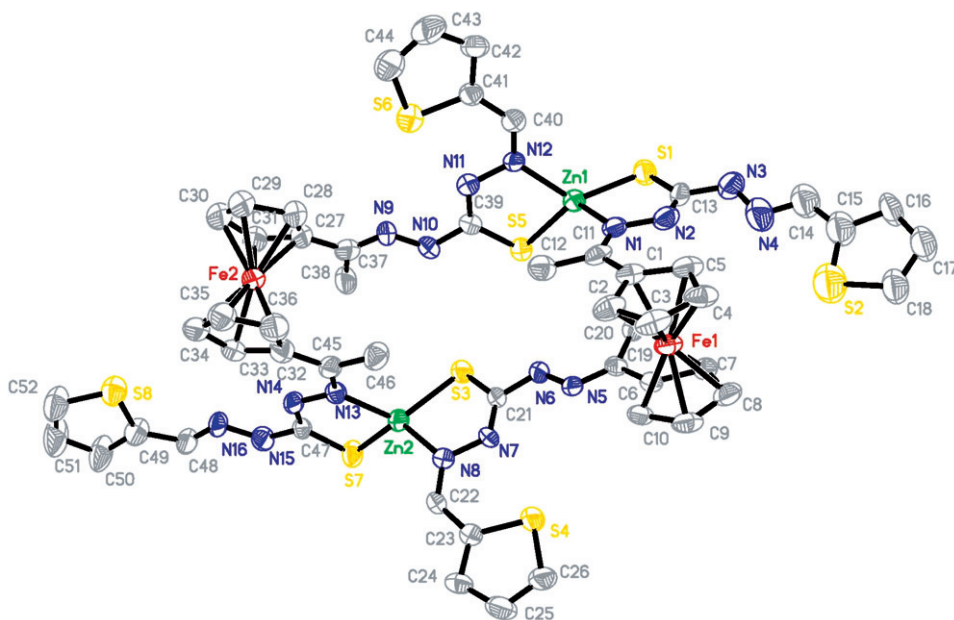


Figure 1. The molecular structure of the complex. The hydrogen atoms are omitted for clarity.

$F(000) = 2928$ . The final refinement by full-matrix least-squares was converged at  $R = 0.0796$  and  $R_w = 0.2119$ .

The crystal data and structure refinement data are given in Supplementary material. Selected bond lengths and angles are given in table 1 and hydrogen bonds are given in table 2.

The binuclear complex  $Zn_2(FcL)_2$  is built as centrosymmetric units (figure 1). Each zinc is four-coordinate by two S and two N atoms from two ligands forming two pentagonal rings  $Zn(1)–N(1)–N(2)–C(13)–S(1)$  and  $Zn(1)–N(12)–N(11)–C(39)–S(5)$  through bridging Zn(II). The dihedral angle between the two planes is  $88.57^\circ$ . The distance of  $C(14)–N(4)$  (0.1240 nm) is shorter than that of the  $C(11)–N(1)$  bond (0.1327(13) nm), because N(4) does not interact with the zinc. Many thiocarbonylhydrazones chelate metal ions forming six-membered rings  $M–N–N–C–N–N$  via the azomethine nitrogens [24]. However, FcL coordinated to Zn(II) forms five-membered chelate rings  $Zn–N–N–C–S$  via the azomethine nitrogens and thiocarbonyl sulfurs. In addition, two zinc ions with two chelate ligands form a 22-membered macroheterocycle through two ferrocenyl bridging ligands. The FcL groups are polydentate

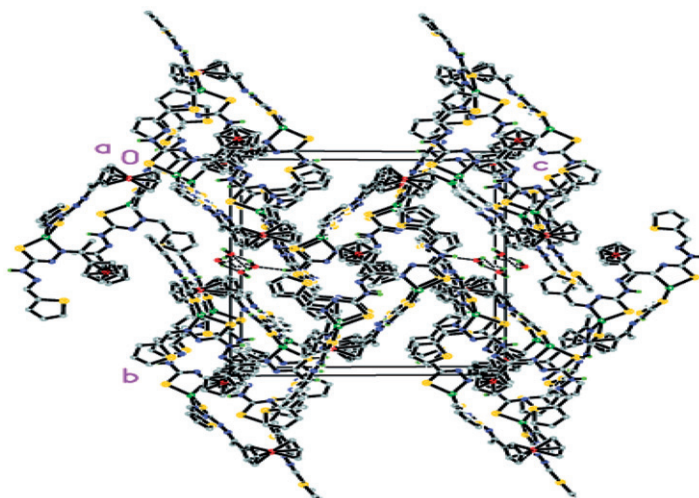


Figure 2. Packing of crystal cell of the complex.

chelating ligands. The Zn(1)–Zn(2) and Fe(1)–Fe(2) distances are 0.7829 and 1.1184 nm, respectively. The dihedral angle between Zn(1)–Fe(1)–Fe(2) and Zn(2)–Fe(1)–Fe(2) rings is 87.44°. From the packing diagram (figure 2), a nano-hole was formed and two waters fill it. The intramolecular hydrogen bonds from the imine with the thiocarbonyl sulfur N(6)–H(6)···S(5)=0.287 nm and N(10)–H(10D)···S(3)=0.300 nm are weak. Intermolecular hydrogen bonds originating from water with water O(1)–H(2W)···O(2)#=0.161 nm, and water with imine N(3)–H(3D)···O(1)#3=0.215 nm are strong. Zn<sub>2</sub>(FcL)<sub>2</sub> units are connected by intermolecular hydrogen bonds (N(15)–H(15)···S(1)#2=0.273 nm) leading to an infinite 1-D- helical chain as shown in figure 3.

### 3.2. Spectroscopy

The important absorptions in the IR spectra of FcL at 3448, 1592, 1520, and 1250 cm<sup>-1</sup> are attributed to  $\nu(\text{N-H})$ ,  $\nu(\text{C=N})$ ,  $\nu(\text{C-C thiophene})$ , and  $\nu(\text{N-N})$ , respectively [25, 26]. In the complex the absorption at 474 cm<sup>-1</sup> is attributed to M–S vibration [27]. Absorptions in the 1302–1225 cm<sup>-1</sup> region shift to shorter wavenumbers and a new strong band at 1652 cm<sup>-1</sup> is observed in the complex [28], perhaps the N–C vibration. In the UV-Vis spectra a broad band centered at 335 nm was noted for the ligand, attributed to a  $\pi-\pi^*$  transition of the azomethine chromophore [29, 30] shifting to 305 nm in the complex indicating that the ligand is coordinated to the Zn(II) ions.

### 3.3. Electrochemical properties

The electrochemical properties of FcL were measured by cyclic voltammetry in acetonitrile at 100 mV s<sup>-1</sup> by using tetrabutyl ammonium perchlorate as the supporting electrolyte in 0.1 M concentration. The  $E_{\text{pa}}$  of FcL is 0.826 V and for the Zn<sup>2+</sup> + FcL

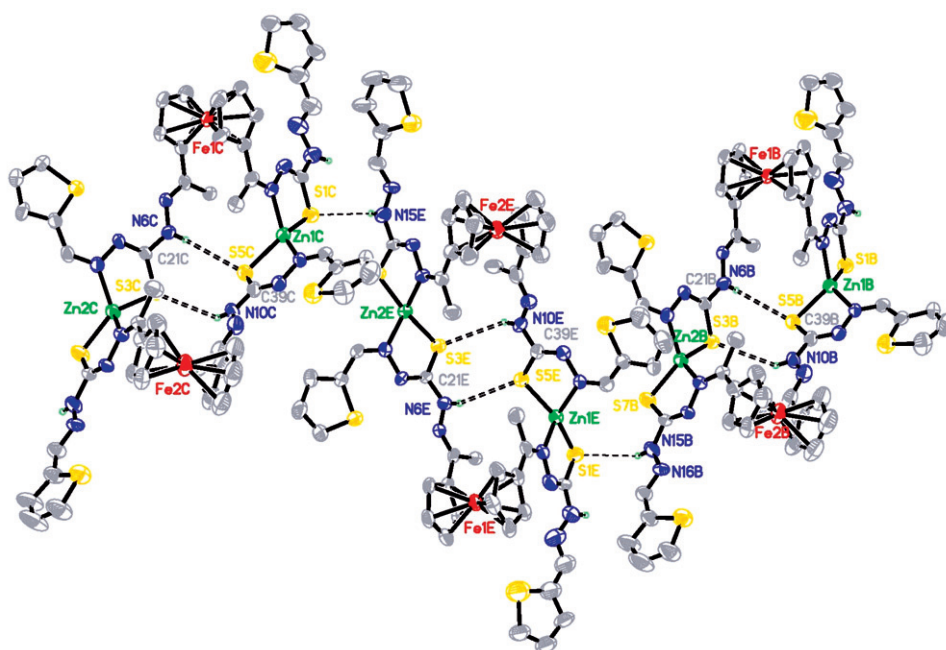


Figure 3. View of the infinite 1-D chain structure of the complex, generated through hydrogen bond interactions.

Table 3. Electrochemical response for FcL vs. transition metal cations in acetonitrile in 0.1 M tetrabutylammonium perchlorate.

Receptor	$\Delta E_{pa}$ (mV)								
	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>	Co <sup>2+</sup>	Mn <sup>2+</sup>	Hg <sup>2+</sup>	Pb <sup>2+</sup>	Ba <sup>2+</sup>
FcL	135	19	15	26	<10	29	38	<10	<10

All potential data refer to the Ag/AgCl electrode at ambient temperature at a scan rate of 100 mV s<sup>-1</sup> in acetonitrile solution using TBAP (0.1 mol L<sup>-1</sup>) as the supporting electrolyte on a GC working electrode, CV recorded from 0.00 to 1.20 V.  $\Delta E_{pa}$  is defined as  $E_{pa}(\text{receptor} + \text{cation}) - E_{pa}(\text{free receptor})$ .

mixtures is 0.961 V. The shift of 135 mV [ $E_{pa}(\text{Zn}^{2+} + \text{FcL}) - E_{pa}(\text{FcL})$ ] indicates that FcL displays a much larger electrochemical shift in the presence of Zn(II). The effect of cation complexation on the electrochemical properties of these receptors was investigated. The redox response of FcL to Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Ba<sup>2+</sup> is much lower. Furthermore, when an equimolar mixture Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Ba<sup>2+</sup> was added to the solution of FcL, the extent of the anodic peak shift is approximately equal to that induced by Zn<sup>2+</sup> alone (the concentration of ligand FcL and metal ions are all 5 × 10<sup>-4</sup> mol L<sup>-1</sup>). This result suggests that in the presence of all these metal ions FcL preferentially coordinates to Zn<sup>2+</sup>. Therefore, FcL is a good candidate for a sensor to detect Zn<sup>2+</sup> (table 3 and figure 4) [31].

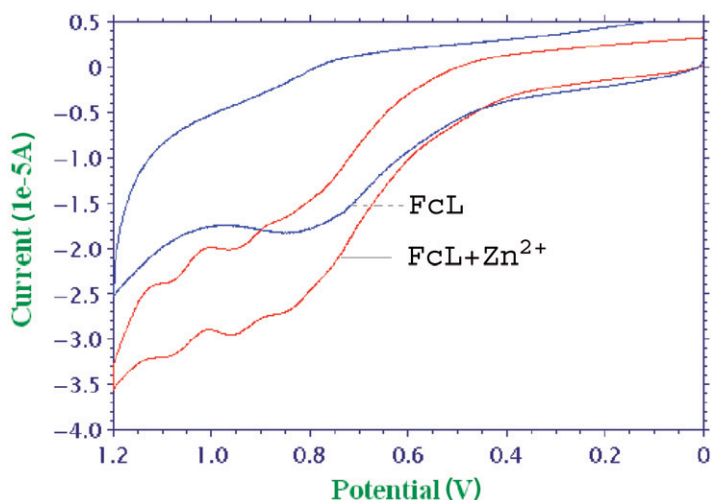


Figure 4. CVs of FcL and FcL + Zn<sup>2+</sup> in acetonitrile.

#### 4. Conclusion

In summary, a new binuclear Zn(II) coordination compound Zn<sub>2</sub>(FcL)<sub>2</sub> has been synthesized; the zinc centers are bonded through ferrocenyl bridging ligands with N, S donors forming a 22-membered macroheterocycle. A combination of coordination properties and suitable redox groups has proven to be a good method to design new receptors for the electrochemical recognition of metal ions in nonaqueous solution. FcL can, through an electrochemical response, detect Zn<sup>2+</sup> in nonaqueous environment; the redox response of FcL to Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Ba<sup>2+</sup> is much lower.

#### Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC-708122, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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