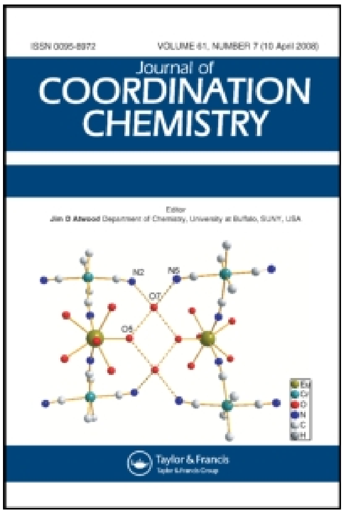

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Crystal structure and electrochemistry of a 2-D polymer with a nano-hole

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Crystal structure and electrochemistry of a 2-D polymer with a nano-hole

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A structure with a nano-hole containing coordination polymer was obtained. X-ray determination shows that it belongs to monoclinic system $P21/n$ space group, with $a = 1.09543(12)$ nm, $b = 1.61279(18)$ nm, $c = 1.43874(16)$ nm, $\beta = 92.8260(10)^\circ$ and final R indices $R = 0.0523$ and $Rw = 0.1440$. It is a uniform zigzag chain with four Zn atoms, two 4,4′-bipyridines and two ferrocenylcarboxylates forming a macrocyclic.

Keywords: Ferrocenylcarboxylate; Crystal structure; Nano-hole; Electrochemical property

1. Introduction

Metallo-macrocycles are important molecular entities, partly because of their role in supramolecular assembly and clathration, promising great potential in molecular sensing technology [1–3]. Many derivatives of these compounds can be prepared by changing the nature of the central metal atom and formally fusing an additional bidentate ligand to the central core [4]. Heteropolymetallic assemblies consisting of the macrocyclic ligands (redox-active centers) and metal ions (Lewis acid) are expected to afford intriguing prospects for small molecule activation. They may serve as multielectron redox mediators in the redox-catalytic reactions. Ferrocene-containing macrocycles and the cryptands have attracted considerable attention due to their potential widespread applications [5]. Ferrocenyl carboxylates are highly versatile molecules for supramolecular construction, as bridging or monodentate ligands, forming binuclear, one-dimensional chain, 2-D layered, and three-dimensional framework structures [6–8]. It can even act as a hydrogen bond acceptor to form hydrogen-bonded supramolecular assemblies. Several examples exist of zinc coordination complexes of ferrocenylcarboxylates [9–14], but seldom producing macrocyclic complexes with 2-D structure.

In the present article, we report the synthesis and structure of a new macrocyclic polymer connecting two ferrocene units via 4,4′-bipyridine bridges and present a study of the electrochemical behavior.

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2. Experimental

2.1. *Materials and physical measurements*

Ferrocenyldicarboxylate was prepared by the previously reported procedure [15, 16]. Other reagents were used as received from commercial suppliers without purification.

IR spectra of the complex were measured on a Perkin–Elmer FTIR-1750 spectrometer. Elemental analyses were performed on a Flash EA 1112. Electrochemical experiments were performed in dry acetonitrile with CHI 650A electrochemical analyzer using a conventional three-electrode system.

2.2. *Synthesis of the coordination polymer*

A methanol solution of $Zn(NO_3)_2$ (2 mL, 0.05 mmol) and 4,4′-bipyridine (2 mL, 0.05 mmol) was added dropwise into a water solution of ferrocenyldicarboxylate (3 mL, 0.05 mmol). The mixture was refluxed 1 h and the precipitated yellow material was filtered off after cooling; light yellow crystals suitable for single-crystal X-ray diffraction analysis were gained by slow evaporation at room temperature for about two weeks. Yield: 38%. IR (KBr, cm^{-1}): 3542m, 3480m, 3090w, 2927w, 1710m, 1611s, 1579s, 1484s, 1415s, 1385s, 1354s, 1218m, 1184w, 1070m, 1029w, 810s, 796m, 731w, 641m, 631m, 561w, 514m, 487m. Anal. Calcd for $C_{24}H_{18}CdFeN_2O_5$: C, 49.47; H, 3.11; N, 4.81%. Found: C, 49.35; H, 3.15; N, 4.75%.

2.3. *Structure determination*

X-ray single-crystal diffraction data for the coordination polymer was collected on a Bruker Smart 1000 CCD diffractometer at 293(2)K with Mo-Kα radiation ($\lambda = 0.071073$ nm). $I > 2\theta$ reflections were 4170. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms are refined anisotropically and hydrogen atoms are included but not refined. The final cycle of full-matrix least-squares refinement is based on observed reflections and variable parameters. All calculations are performed using the SHELXL-97 crystallographic software package [17] and refined by full-matrix least-squares methods based on F^2 with isotropic thermal parameters for the non-hydrogen atoms. The crystal data and selected parameters are given in tables 1 and 2.

3. Results and discussion

3.1. *Structure description*

The crystal structure (figure 1) belongs to the monoclinic system $P21/n$ space group, with $a = 1.09543(12)$ nm, $b = 1.61279(18)$ nm, $c = 1.43874(16)$ nm, $\beta = 92.8260(10)^\circ$, $V = 2538.7\,\text{Å}^3$, $Z = 4$, $D_{\text{Calcd}} = 1.564\,\text{Mg m}^{-3}$, crystal size $0.28 \times 0.19 \times 0.11\,\text{mm}^3$, $F(000) = 1232$. The final refinement by full-matrix least-squares was converged at $R = 0.0523$ and $Rw = 0.1440$. Selected bond lengths and angles are given in table 2 and hydrogen bonds are given in table 3.

Table 1. Crystal data and structure refinement for the polymer.

Empirical formula	$C_{23}H_{28}FeN_2O_9Zn$
Formula weight	597.69
Temperature (K)	291(2)
Wavelength (nm)	0.071073
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions (nm, °)	
a	1.09543(12)
b	1.61279(18)
c	1.43874(16)
β	92.8260(10)
Volume (Å^3)	2538.7
Z	4
D_{Calcd} (Mg m^{-3})	1.564
Absorption coefficient (mm^{-1})	1.570
$F(000)$	1232
Crystal size (mm^3)	0.28 × 0.19 × 0.11
θ range for data collection (°)	2.25 to 28.31
Limiting indices	$-14 \leq h \leq 14$, $-21 \leq k \leq 21$, $-19 \leq l \leq 18$
Reflections collected/unique	20834/6276 [$R_{(int)} = 0.0426$]
Completeness to θ	99.3%
Absorption correction	None
Max. and min. transmission	0.8463 and 0.6632
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6276/187/326
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\theta$]	$R_1 = 0.0523$, $wR_2 = 0.1440$
R indices (all data)	$R_1 = 0.0848$, $wR_2 = 0.1641$
Largest diff. peak and hole (e Å^{-3})	943 and 922

Table 2. Selected bond distances (nm) and angles (°) for the complex.

Zn(1)–O(1)	0.1973(2)	Zn(1)–N(2)#1	0.2087(2)
Zn(1)–N(1)	0.2090(2)	Zn(1)–O(3)#2	0.2143(2)
Zn(1)–O(4)#2	0.2216(3)	Zn(1)–C(18)#2	0.2518(3)
O(3)–C(18)	0.1258(4)	O(3)–Zn(1)#3	0.2143(2)
O(4)–C(18)	0.1237(4)	O(4)–Zn(1)#3	0.2216(3)
O(1)–Zn(1)–N(2)#1	97.87(8)	O(1)–Zn(1)–N(1)	97.05(8)
N(2)#1–Zn(1)–N(1)	97.27(9)	O(1)–Zn(1)–O(3)#2	155.46(10)
N(2)#1–Zn(1)–O(3)#2	96.43(9)	N(1)–Zn(1)–O(3)#2	100.80(9)
O(1)–Zn(1)–O(4)#2	100.91(9)	N(2)#1–Zn(1)–O(4)#2	152.00(9)
N(1)–Zn(1)–O(4)#2	100.81(9)	O(3)#2–Zn(1)–O(4)#2	59.32(9)
O(1)–Zn(1)–C(18)#2	129.40(10)	N(2)#1–Zn(1)–C(18)#2	125.59(10)
N(1)–Zn(1)–C(18)#2	101.14(9)	O(3)#2–Zn(1)–C(18)#2	29.96(10)
O(4)#2–Zn(1)–C(18)#2	29.41(10)		

The coordination environment of Zn(II), shown in figure 1, is five-coordinate by three oxygens of carboxyl from different ferrocene groups, and two nitrogens of different 4,4′-bipyridines, forming a distorted square pyramid. The bottom plane is composed of O1–O3a–O4a–N2a with average deviation of 0.00069 nm from the plane. The distance from N1 to bottom is 0.24041 nm, and the Zn(II) atom is 0.03169 nm above the bottom. The angle between two pyridine planes is 87.3° subvertical.

The molecular structure (figure 2) consists of uniform zigzag chains in which neighboring Zn atoms are connected through 4,4′-bipyridine bridges, and the 1,1′-ferrocenedicarboxylates link the chains to form a two-dimensional network.

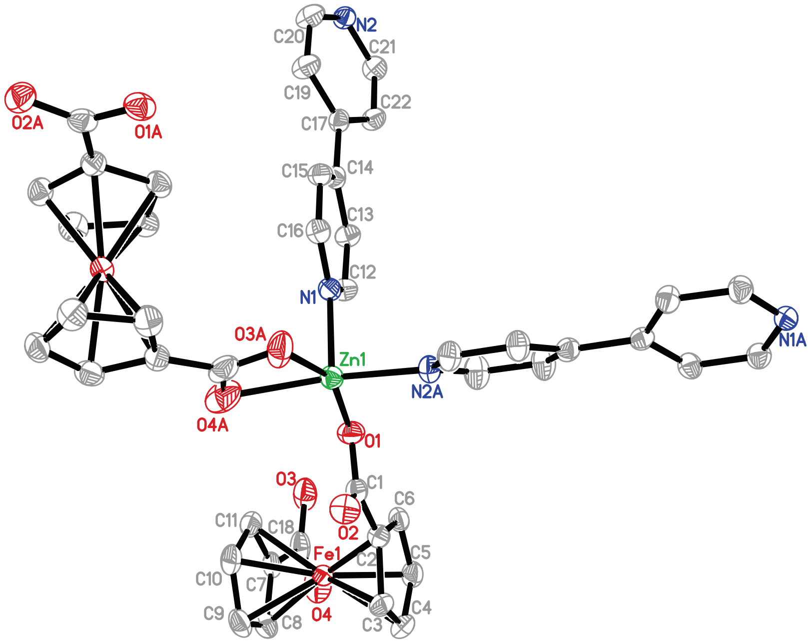

Figure 1. The coordination environment of Zn with atom labeling scheme (30% thermal ellipsoid).

Table 3. Hydrogen bonds for the coordination polymer (nm and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(5)–H(5A)···O(4)#5	0.082	0.227	0.2707(6)	113.9
O(6)–H(1W)···O(7)#6	0.085	0.220	0.2769(6)	124.2
O(6)–H(2W)···O(9)#2	0.085	0.192	0.2761(8)	172.7
O(7)–H(4W)···O(2)	0.085	0.201	0.2859(4)	179.6
O(7)–H(3W)···O(7)#7	0.084	0.202	0.2768(9)	148.5
O(8)–H(5W)···O(6)#8	0.084	0.193	0.2750(5)	168.3
O(8)–H(6W)···O(2)#9	0.084	0.202	0.2853(4)	172.8
O(9)–H(7W)···O(6)#3	0.085	0.230	0.2761(8)	114.6

The carboxylate groups function in both bidentate and monodentate chelating modes. Four Zn atoms, two 4,4′-bipyridines and two ferrocenylcarboxylates form a macrocycle. The Fe–Fe distance is 1.6729 nm. Four zinc ions form a rectangle with 0.9211 nm and 1.1244 nm sides. From the packing diagram (figure 3), a nano-hole was formed with water and methanol filling the hole. The solvent molecules are linked through strong inter-molecular hydrogen bonds (table 3), and two waters form hydrogen bonds with ferrocenylcarboxylate, O(7)–H(4W)···O(2) 0.2859(4) nm, 179.6°; O(8)–H(6W)···O(2) #9 0.2853(4) nm, 172.8°; the solvents are very stable in the crystal.

3.2. *Electrochemistry*

The cyclic voltammetric behavior of the coordination polymer shows one quasi-reversible redox wave in the potential range of 0.3–1.0 V at the GC electrode, attributed

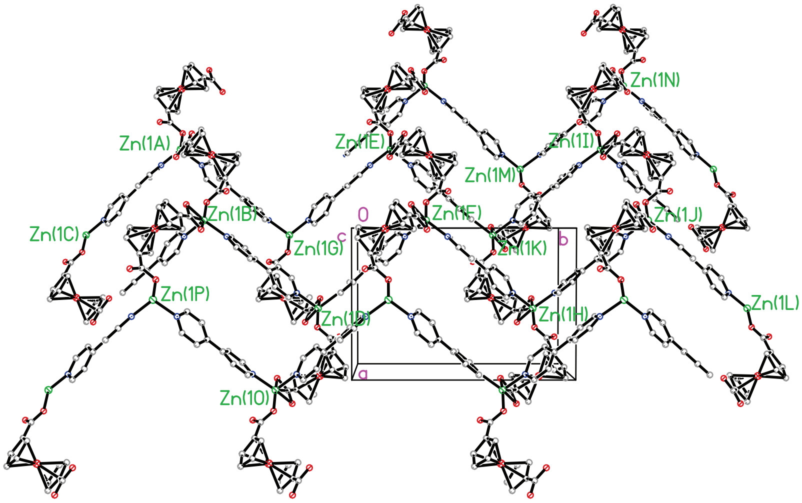

Figure 2. Two-dimensional structure of the coordination polymer.

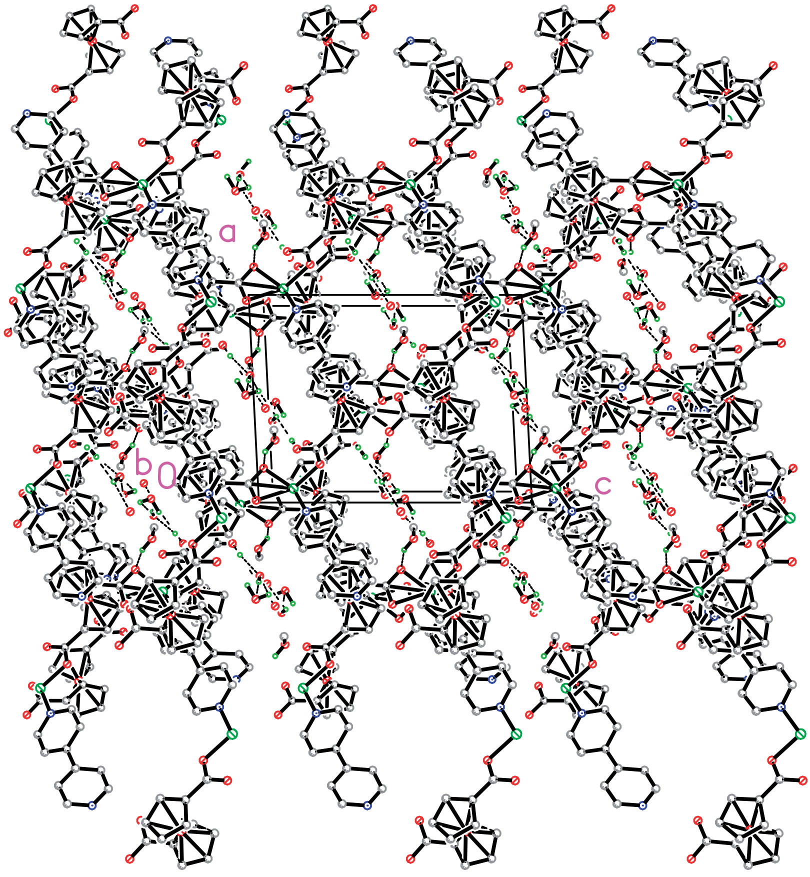

Figure 3. Packing diagram of the coordination polymer.

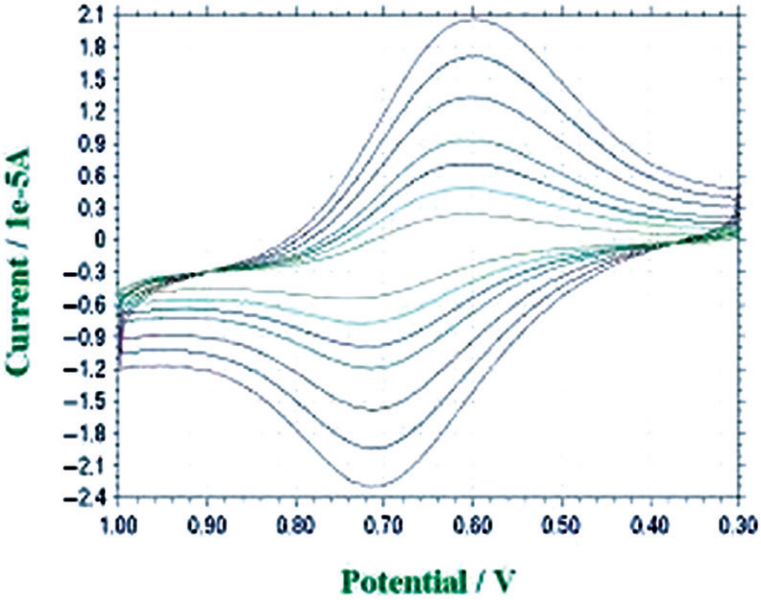

Figure 4. CVs of complex ($5 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) at a GC electrode in 0.1M TBAP acetonitrile at different scan rates.

to the Fc/Fc$^+$ redox process. The formal potential ($E^0 = 0.65\,\mathrm{V}$), taken as the average of E_{pa} and E_{pc} is larger than ferrocene ($E^0 = 0.44\,\mathrm{V}$) and slightly lower than ferrocenyldicarboxylate ($E^0 = 0.68\,\mathrm{V}$), suggesting that the electron-withdrawing carboxylate group significantly influences the redox potential of the iron center [18]. Electrochemical reversibility is judged by analysis of the CVs, varying both scan rate(υ) and concentration, with symmetrical redox waves (figure 4). In addition, i_p is linearly proportional to $\upsilon^{1/2}$, confirming the reversible diffusion-controlled process for the Fc$^+$/Fc system.

4. Conclusion

A new Zn(II) complex with mixed chelating and bridging ligands has been synthesized, its structure determined and its electrochemistry examined.

Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC-635065, 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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