Synthesis and characterization of Cu(II), Ni(II), and Fe(III) complexes of 5-(8-ethoxycarbonyl-1-naphthyl)-10,15,20-triphenyl porphyrin

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Synthesis and characterization of Cu(II), Ni(II), and Fe(III) complexes of 5-(8-ethoxycarbonyl-1-naphthyl)-10,15,20-triphenyl porphyrin

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We have synthesized three complexes of 5-(8-ethoxycarbonyl-1-naphthyl)-10,15,20-triphenyl porphyrin (ENTPP), [Cu(ENTPP)], [Ni(ENTPP), and [Fe(ENTPP)Cl]. X-ray crystallography reveals that copper and nickel species are four-coordinate, while the iron complex is five-coordinate. The porphyrin in all the three species maintains similar conformations, in which rotational hindrance makes the ester group at the 8-position of naphthyl lie above the porphyrin plane leading to axial chirality in the single molecule. However, only chiral crystals of [Cu(ENTPP)] were obtained by spontaneous resolution upon crystallization, while [Ni(ENTPP) and [Fe(ENTPP)Cl] were obtained as achiral crystals of racemic compounds. CD spectra have also confirmed the chirality of the crystalline samples. The origin of CD signals has also been discussed.

Keywords: Chiral porphyrin; Naphthyl; Spontaneous resolution; Crystal structure

1. Introduction

Chiral porphyrins are of particular interest in molecular recognition, asymmetric catalysis, and nonlinear optics [1]. One kind of common chiral porphyrin contains stereogenic centers, but another kind of chiral porphyrins does not contain such chiral substituents. Instead these chiral porphyrins have various substituents appended onto the rigid porphyrin framework [2]. The method to make such porphyrins will usually lead to achiral crystals of racemic mixtures. Only 5–10% of all racemates are known to crystallize as conglomerates [3]. In our previous studies, we have synthesized a 5-(8-ethoxycarbonyl-1-naphthyl)-10,15,20-triphenyl porphyrin (H$_2$ENTPP) [4]. In that case, the 8-position ester lies above the porphyrin plane and leads to axial chirality because of the steric constraints. Spontaneous resolution of enantiomers occurred during crystallization of H$_2$ENTPP, producing crystals for which a CD signal was registered.


Since crystals of free H_2ENTPP can be solved by spontaneous resolution, could its metal complexes? One way is to obtain an isomorphic structure of H_2ENTPP, but it is not a common phenomenon and difficult to control. If only the NH protons are replaced by metal, the overall structure could maintain similar geometry as the free base, making it possible to obtain isomorphic crystals of H_2ENTPP. Such arrangement requires four-coordinate square planar geometry for the metal, common for Cu(II) and Ni(II) porphyrinates. We synthesized [Cu(ENTPP)] and [Ni(ENTPP)] in current studies as shown in scheme 1. Besides four-coordinate species, we have also made five-coordinate iron(III) using the same porphyrin. Single crystals of the three complexes have been obtained and characterized by X-ray crystallography. Chiral crystalline samples of [Cu(ENTPP)] have been spontaneously resolved upon crystallization; the other two species grow in achiral space groups. Their corresponding ^1H NMR and circular dichroism (CD) spectra have also been characterized.

2. Experimental

2.1. *General procedures*

2.1.1. Materials and general methods.   All reagents were of analytical grade and used without purification. Anhydrous THF was dried and redistilled over sodium benzophenone ketyl. All solvents were used as received. H_2ENTPP was prepared according to literature procedure [4]. UV–vis spectra were measured on a Shimadzu UV-3150 spectrometer. CD
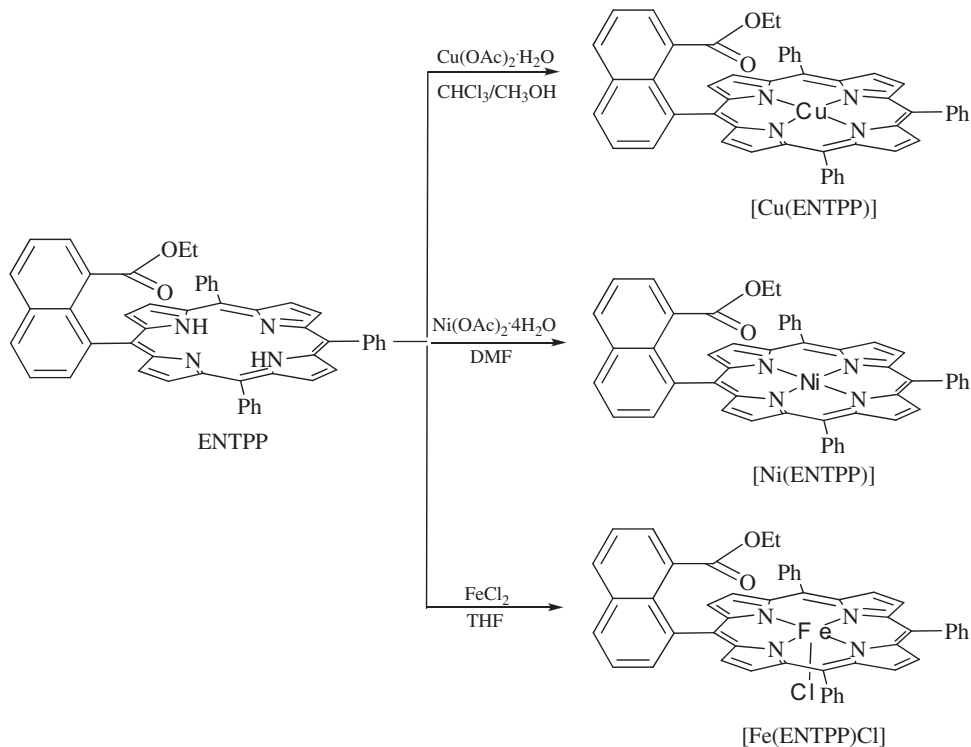
Scheme 1.   Synthetic route to [Cu(ENTPP)], [Ni(ENTPP)], and [Fe(ENTPP)Cl].

spectroscopy was performed with an AVIV 410 spectrophotometer in dry KBr pellets. ^{1}H NMR spectra were carried out using Bruker AVANCE 400 and 300 spectrometers in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Mass spectra were taken with an Agilent 6220 Accurate-Mass TOF LC/MS.

2.2. *Synthesis of metallic complexes*

2.2.1. Synthesis of [Cu(ENTPP)]. [Cu(ENTPP)] was prepared according to literature procedure [5]. To a solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.13 g, 0.65 mM) in methanol (5 mL), solution of H_2ENTPP (0.22 g, 0.30 mM) in chloroform (40 mL) was added. The mixture was refluxed for 2 h. After the solution was cooled to room temperature, it was washed with water (3×100 mL). The organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The resulting solid was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (1 : 1 v/v) as the eluent. A light purple solid was obtained; yield 0.23 g (95%). LC-ESI-MS: m/z calcd for $C_{51}H_{34}N_4O_2Cu$ 797.20; found 798.20 $[M + H]^+$. UV–vis (CH_2Cl_2): λ_{max}, nm ($M^{-1} cm^{-1}$): 419(4.77×10^4), 541 (2.11×10^3). Anal. Calcd for $C_{51}H_{36}N_2O_2Cu$ (%): C, 76.72; H, 4.29; N, 7.02. Found: C, 76.52; H, 4.29; N, 6.99. Suitable crystals for X-ray crystallography were obtained by slow evaporation of its solution in a mixture of methylene chloride and hexane.

2.2.2. Synthesis of [Ni(ENTPP)]. [Ni(ENTPP)] was prepared according to literature procedure [6]. To a refluxing solution of H_2ENTPP (0.18 g, 0.24 mM) in DMF, Ni$(CH_3COO)_2 \cdot 4H_2O$ (0.142 g, 0.57 mM) was added. The mixture was refluxed for 5 h. After the solution was cooled to room temperature, it was washed with water (6×100 mL). The organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The resulting solid was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (1 : 1 v/v) as the eluent. A light red solid was obtained; yield 0.13 g (89%). LC-ESI-MS: m/z calcd for $C_{51}H_{34}N_4O_2Ni$ 792.20; found 793.21 $[M + H]^+$. UV–vis (CH_2Cl_2): λ_{max}, nm ($M^{-1} cm^{-1}$): 417(2.67×10^4), 531(2.03×10^3). Anal. Calcd for $C_{51}H_{34}N_2O_2$-Ni·$0.1CH_2Cl_2$ (%): C, 76.52; H, 4.30; N, 6.99. Found: C, 76.52; H, 4.35; N, 6.98. ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.73(4H, s), 8.67(2H, d), 8.56(2H, d), 8.41(1H, d), 8.24(1H, d), 8.15(1H, d), 8.03(4H, s), 7.87(2H, t), 7.67(10H, m), 7.48(1H, t), 7.24(1H, s), 1.15(2H, m), −0.72(3 H, t). Suitable crystals for X-ray crystallography were obtained by slow diffusion of its solution in toluene by methanol.

2.2.3. Synthesis of [Fe(ENTPP)Cl]. [Fe(ENTPP)Cl] was prepared according to literature procedure [6]. To a 200-mL Schlenk tube containing H_2ENTPP (0.22 g, 0.30 mM) and anhydrous $FeCl_2$ (2 g, 0.016 mol), dry THF (100 mL) and pyridine (380 μL) were added. The mixture was refluxed overnight, cooled to room temperature, and then filtered by sintered glass funnel. The solvent was removed in vacuo, and the resulting solid was purified by column chromatography on silica gel with methanol/CH_2Cl_2 (1 : 100 v/v) as the eluent. A light black solid was obtained; yield 0.21 g (89%). Anal. Calcd for $C_{51}H_{34}ClFeN_4O_2 \cdot 0.5CH_2Cl_2$ (%): C, 74.24; H, 4.23; N, 6.72. Found: C, 74.61; H, 4.55; N, 6.67. UV–vis (CH_2Cl_2): λ_{max}, nm ($M^{-1} cm^{-1}$): 379(3.9×10^4), 419(7.74×10^4), 512

(9.18 × 10^3), 589(1.98 × 10^3) 695(1.7 × 10^3). LC-ESI-MS: *m/z* calcd for C$_{51}$H$_{34}$ClFe N$_4$O$_2$825.17; found 790.20 [M–Cl]$^+$. Suitable crystals for X-ray crystallography were obtained by slow diffusion of its solution in toluene by hexane.

2.3. *X-ray crystallography*

X-ray data were collected at 223(2) K with a Rigaku Mercury CCD diffractometer using Mo K radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 using full matrix least-squares with SHELXTL version 97 [7]. All non-hydrogen atoms were refined anisotropically. Hydrogens were added in calculated positions and refined as riding on their parent. Crystallographic details, atomic coordinates, anisotropic thermal parameters, and hydrogen coordinates are given in the cif file. In [Cu(ENTPP)] the asymmetric unit consists of one molecule of the complex and one hexane molecule. [Ni (ENTPP)] and [Fe(ENTPP)Cl] also crystallize as solvates. Due to extensive solvent disorder, contributions of solvent molecules were removed from the diffraction data with SQUEEZE [8]. In [Ni(ENTPP)], 107 electrons were found in two voids (overall volume 657 Å^3), which corresponds to roughly 1.5 molecules of CH$_3$OH per asymmetric unit. In [Fe(ENTPP)Cl], 159 electrons were found in two voids (overall volume 780 Å^3), which corresponds to roughly 0.8 molecules of toluene per asymmetric unit. Brief crystal data for the three complexes are listed in table 1.

3. Results and discussion

[Cu(ENTPP)], [Ni(ENTPP)], and [Fe(ENTPP)Cl] have been synthesized as shown in scheme 1. For spontaneous resolution, crystallization methods are very important, but related to many factors, and very difficult to control. We tried to grow crystals of [Cu (ENTPP)] and [Ni(ENTPP)] using the same method as that for H$_2$ENTPP. For Cu(II) species, we obtained chiral crystals, but for Ni(II), unfortunately, we did not obtain suitable single crystals for X-ray crystallography. So we tried other crystallization solvents. When we slowly diffused methanol into its solution in toluene, achiral single crystals of Ni(II) were obtained. For [Fe(ENTPP)Cl], we also tried different methods, only hexane/toluene system provided suitable single crystals.

3.1. *Molecular structure*

[Cu(ENTPP)]·C$_6$H$_{14}$ crystallizes in a chiral space group *P2$_1$* and is isomorphic with H$_2$ENTPP·C$_6$H$_{14}$ [4]. The refinements suggest the single crystal of [Cu(ENTPP)] forms racemic twins. In this case, the enantiomorphic domains were of different volume (0.71 : 0.29). The structure of the dominant component is shown in figure 1. Cu(II) inserted into the porphyrin core, coordinated by four pyrrole nitrogens, and is coplanar with the four nitrogen (the displacement out of four nitrogen plane is 0.01 Å). Selected distances are listed in table 2. The average Cu–N$_p$ distance is 1.997(6) Å, typical of Cu–N bond lengths found in planar copper porphyrinates [9]. Except for Cu(II), other data very much resemble those of H$_2$ENTPP. The porphyrin has one mononaphthyl group and three phenyl groups at *meso*-positions. The rigid structure makes the 8-position substituent, an ester group, lie above the porphyrin plane. Because of the steric constraint, the ester group is

Table 1. Crystallographic data for the complexes.

Compound	[Cu(ENTPP)]·C_6H_{14}	[Ni(ENTPP)]·1.5CH$_3$OH	[Fe(ENTPP)Cl]·0.8C$_6$H$_5$CH$_3$
Empirical formula	$C_{57}H_{48}CuN_4O_2$	$C_{51}H_{34}N_4NiO_2$	$C_{51}H_{34}ClFeN_4O_2$
Formula weight (g mol^{-1})	884.53	793.53	826.12
Temperature (K)	223(2)	223(2)	223(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1/c$
Unit cell dimensions	$a = 10.658(2)$ Å	$a = 23.032(5)$ Å	$a = 11.096(2)$ Å
	$b = 12.105(2)$ Å	$b = 12.184(2)$ Å	$b = 16.521(3)$ Å
	$c = 17.769(4)$ Å	$c = 15.299(3)$ Å	$c = 24.589(10)$ Å
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 103.33(3)°$	$\beta = 100.06(3)°$	$\beta = 99.48(3)°$
	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$
Volume (Å^3)	2230.7(8)	4227.2(14)	4446.1(15)
Z	2	4	4
ρ (g cm^{-3})	1.317	1.247	1.234
F(000)	926	1648	1708
Crystal size (mm^3)	$0.39 \times 0.35 \times 0.24$	$0.50 \times 0.20 \times 0.10$	$0.50 \times 0.20 \times 0.10$
Theta range for data collection	3.02–25.00°	3.17–25.00°	3.09–25.00°
Limiting indices	$-11 \leqslant h \leqslant 12$	$-24 \leqslant h \leqslant 27$	$-13 \leqslant h \leqslant 11$
	$-14 \leqslant k \leqslant 13$	$-14 \leqslant k \leqslant 12$	$-19 \leqslant k \leqslant 18$
	$-21 \leqslant l \leqslant 17$	$-18 \leqslant l \leqslant 13$	$-27 \leqslant l \leqslant 29$
Reflections collected/unique	11,096/7109	20,050/7406	30,519/7795
Completeness to theta = 25.00°	99.3%	99.4%	99.6%
Data/restraints/parameters	7109/1/557	7406/0/524	7795/3/533
GOF	1.102	1.156	1.125
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0590$	$R_1 = 0.1303$	$R_1 = 0.1154$
	$wR_2 = 0.1448$	$wR_2 = 0.3120$	$wR_2 = 0.2885$
R_1, wR_2 (all data)	$R_1 = 0.0705$	$R_1 = 0.1977$	$R_1 = 0.1762$
	$wR_2 = 0.1538$	$wR_2 = 0.3600$	$wR_2 = 0.3262$
Largest diff. peak and hole (e Å^{-3})	0.335 and -0.373	0.817 and -0.526	0.787 and -0.651

$R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$; $wR_2 = \sum[w(|F_0|^2 - |F_c|^2)^2/\sum w(|F_0|^2)^2]^{1/2}$.

rotationally hindered, which leads to axial chirality in the single molecule (there is one axis of chirality along the bond between the ester group and the naphthalene system) (1d). According to the Cahn–Ingold–Prelog priority rules [10], the single porphyrin has Sa configuration. As shown in figure 2, in the packing structure, there are π–π interactions between the chelating ring in each porphyrin (formed by Cu(1), N(1), N(2), C(A2), (C(A3), and C(M1)) and the part of naphthyl ring (C(14a), C(15a) C(16a), C(17a), C(18a), C(19a), symmetry operator a: $-X$, $0.5 - Y$, $-Z + 2$) in its symmetry related neighboring porphyrin along 2_1 axis (parallel to the b axis). The corresponding center to center distance is 3.928 Å, dihedral angle is 30.9°, and the N(2)···C(15a) distance is 3.462 Å. Such interactions extend along the b axis to form a 1-D assembly as shown in figure S5 of supporting information. The adjacent Cu(II) to Cu(II) distance is 10.75 Å in such assembly. Sheets with the same chirality are arranged parallelly, which results in a chiral crystal.

Despite the chirality in the solid state, there was no observable signal when a single crystal was dissolved in solution. It is possible that racemization is difficult due to intermolecular interactions in the packing structure, but in solution, conversions between conformers of porphyrin are possible and racemization could occur.

For [Ni(ENTPP)] as shown in figure 3, the crystal data are not good, but provide the following useful informations: (1) Ni(II) is coordinated by four pyrrole nitrogens to form a
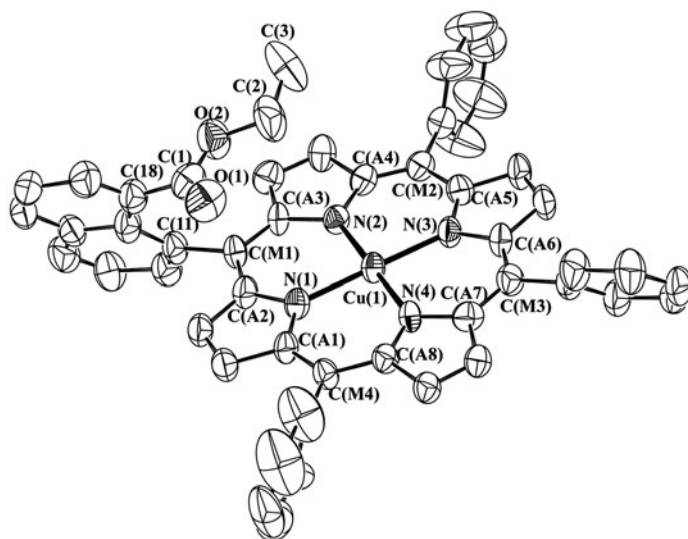
Figure 1.   ORTEP view for [Cu(ENTPP)] at 50% probability thermal ellipsoids. Hydrogens have been omitted for clarity.

Table 2.   Selected bond distances for [Cu(ENTPP)] (Å).

Cu(1)–N(1)	1.995(5)	Cu(1)–N(2)	2.003(4)
Cu(1)–N(3)	1.996(5)	Cu(1)–N(4)	1.991(5)
N(1)–C(A1)	1.393(8)	N(1)–C(A2)	1.380(7)
N(2)–C(A3)	1.390(7)	N(2)–C(A4)	1.370(8)
N(3)–C(A5)	1.369(8)	N(3)–C(A6)	1.389(7)
N(4)–C(A7)	1.384(7)	N(4)–C(A8)	1.393(7)
C(1)–O(1)	1.208(8)	C(1)–O(2)	1.329(9)
C(2)–O(2)	1.459(9)	C(2)–C(3)	1.499(14)

square planar geometry. Ni(II) is diamagnetic, evidenced by NMR studies (*vide infra*). (2) The single porphyrinate molecule is chiral as that in [Cu(ENTPP)]. However, the whole crystal is achiral because it consists of pairs of enantiomers in the achiral space group, $P2_1/c$.

The structure of [Fe(ENTPP)Cl] is much different from both the copper and nickel species. In this case, iron(III) is five-coordinate as shown in figure 4. Beside four pyrrole nitrogen, iron is also coordinated by a chloride. Iron is not in the porphyrin plane, but out of four nitrogen plane with displacement of 0.47 Å. The average Fe–N_p distance is 2.061 (7) Å, which is similar to those in [Fe(TPP)Cl] [11] and related species [12]. The large iron displacement and long Fe–N_p distance suggest iron(III) is high-spin. Fe–Cl distance is 2.224(2) Å. Chloride and ester group are on two sides of the porphyrin plane, avoiding repulsion between them. Similar to [Ni(ENTPP)], the single porphyrinate is chiral, but the whole crystal is achiral.

3.2. *^{1}H NMR spectra*

^{1}H NMR spectra for the porphyrinates have been measured as shown in figure 5. Ni(II) is diamagnetic in the square planar complex [Ni(ENTPP)], while Cu(II) and Fe(III) are
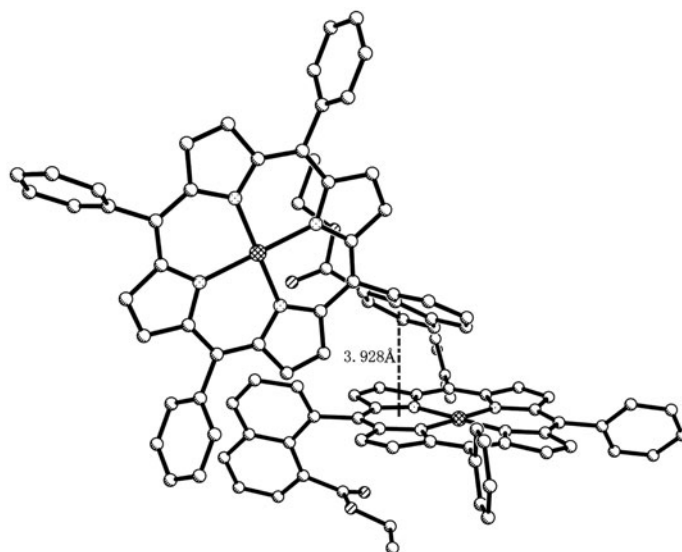
Figure 2. π–π interaction between the chelating ring in each porphyrin (formed by Cu(1), N(1), N(2), C(A2), (C(A3), C(M1)) and part of the naphthyl ring (C(14a), C(15a) C(16a), C(17a), C(18a), C(19a), symmetry operator a: $-X$, $0.5 - Y$, $-Z + 2$)) in its symmetry related neighboring porphyrin. The corresponding center to center distance is 3.928 Å, dihedral angle is 30.9° and the N(2)$\cdots$C(15a) distance is 3.462 Å.
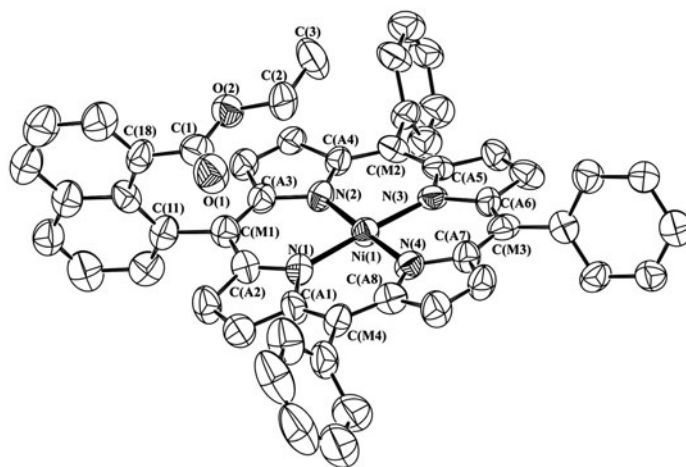

Figure 3. ORTEP view for [Ni(ENTPP)] at 50% probability thermal ellipsoids. Hydrogens have been omitted for clarity.

paramagnetic in [Cu(ENTPP)] and [Fe(ENTPP)Cl]. So, the spectrum for [Ni(ENTPP)] is similar to that for H$_2$ENTPP, with narrow resonance signals and hyperfine structure (*vide supra*). Due to the ring current effect, the signals of eight β-protons in the deshielding region are located at 8.73, 8.67, and 8.56 ppm, similar to the corresponding values for *meso*-5,10,15,20-tetraphenylporphyrin [13]. Signals of two protons at 1.12 ppm and three protons at −0.72 ppm are assigned to an ethyl, shifted upfield by 3.34 and 2.16 ppm
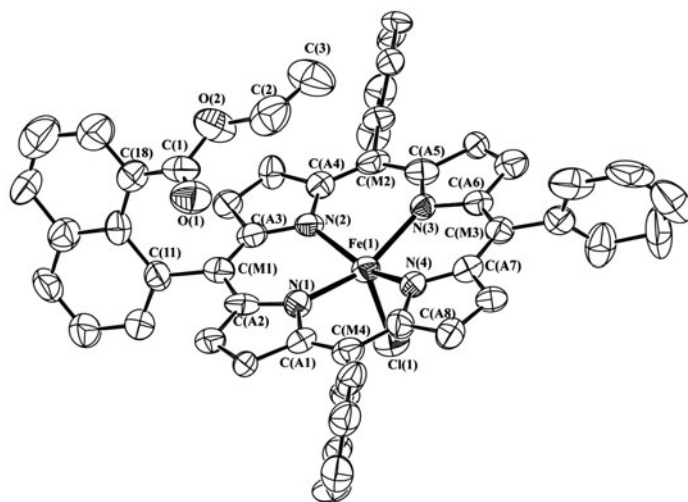
Figure 4. ORTEP view for [Fe(ENTPP)Cl] at 50% probability thermal ellipsoids. Hydrogens have been omitted for clarity.

compared with naphthalene-1-carboxylic acid ethyl ester [14]. This suggests the ethyl is located above the porphyrin plane in solution with the ring current shielding causing upfield shifts.

For the paramagnetic Fe(III) and Cu(II), the signals are broader and expanded. For [Fe(ENTPP)Cl], the spectrum shows resonances in the far-downfield region at 81.30 ppm assigned to the pyrrole protons. It is typical for five-coordinate high-spin (tetraphenyl-porphyrinato)iron(III) complex [15]. For [Cu(ENTPP)], the spectrum is less expanded. Similar to the Cu(II) porphyrinates reported by Goff *et al.* [15, 16], the resonances of eight β-protons for [Cu(ENTPP)] are too broad to be observed. The signals at 7–9 ppm belong to phenyl protons. The resonances at −0.67 and 0.16 ppm are assigned to ethyl.

3.3. *CD spectra*

X-ray crystallography reveals that in the single crystals of [Cu(ENTPP)] there are racemic twins, one enantiomorphic component is in excess, while those of [Ni(ENTPP)] and [Fe(ENTPP)Cl] are achiral. CD spectroscopy further confirms this observation. Several pieces of single crystals were randomly picked and KBr pellets were prepared by grinding each crystal sample with solid potassium bromide (KBr) and applying great pressure to the dry mixture. For [Ni(ENTPP)] and [Fe(ENTPP)Cl], no observable signals were obtained. But for [Cu(ENTPP)], the measured spectra exhibited remarkable CD absorption in Soret band region, which clearly shows strong positive or negative absorptions at 435 nm. Spectra of two selected single crystals are present in figure 6. It confirms that chirality is maintained in single crystals. Such enantiomeric CD spectra provide evidence that one enantiomorphic component is in excess in the solid state.

The CD signals of [Cu(ENTPP)] are very similar to that of H_2ENTPP [4]. Such bisignate Cotton effect is typical in many exciton coupling cases [17]. There is structural similarity between our porphyrin and monomeric porphyrin system bearing two naphthol
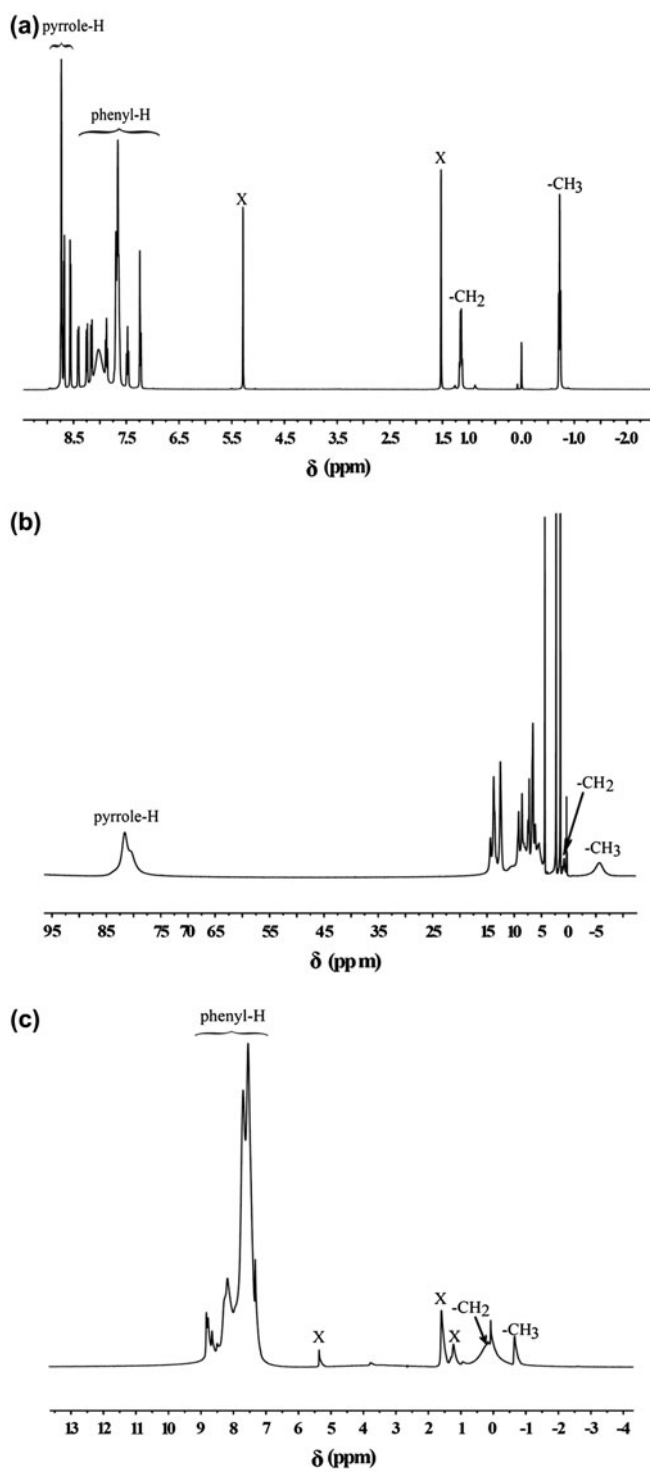
Figure 5. ¹H NMR spectra in CDCl₃ (a) [Ni(ENTPP)] (b) [Fe(ENTPP)Cl] (c) [Cu(ENTPP)]. X, impurity.
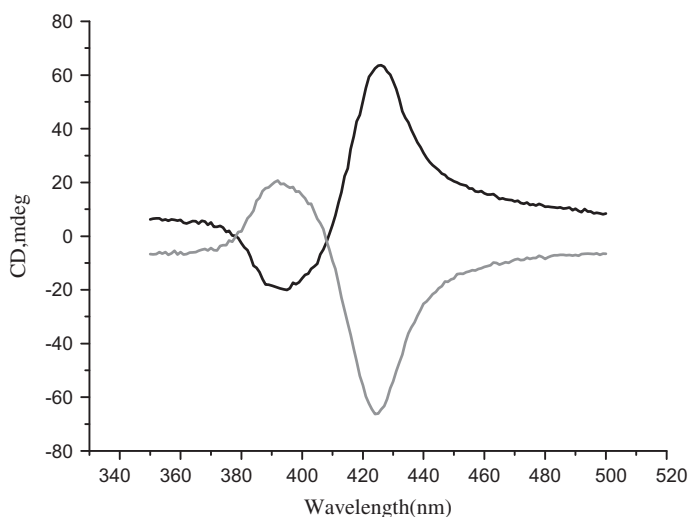
Figure 6. CD spectra of crystallites of [Cu(ENTPP)] in KBr pellets. The two pellets were prepared using selected crystals, and showed enantiomeric CD patterns.

groups reported by Ogoshi and Mizutani [18]. Their proposed mechanism suggested the induced CD was caused by coupling between the magnetic transition dipole moment of the carbonyl group of the guest molecule and the electric transition dipole moment of the Soret band of the porphyrin host. In our system, there are two chromophores, porphyrin plane and carbonyl group, which have similar geometry as in Mizutani's case. So, the bisignate signals are probably caused by coupling between these two chromophores. But, we cannot completely rule out the contributions from intermolecular interaction between porphyrin units in solid state.

4. Conclusion

We have synthesized three metal complexes, [Cu(ENTPP)], [Ni(ENTPP), and [Fe(ENTPP) Cl]. Copper and nickel species are four-coordinate, while the iron complex is five-coordinate. Chiral crystals of [Cu(ENTPP)] were obtained by spontaneous resolution upon crystallization, while only achiral crystals of [Ni(ENTPP) and [Fe(ENTPP)Cl] were obtained. X-ray crystallography reveals that the single porphyrin in each complex is chiral. For individual single crystal of [Cu(ENTPP)], all porphyrin molecules have the same handedness. But for [Ni(ENTPP)] and [Fe(ENTPP)Cl], the existence of pairs of enantiomers lead to achiral crystals. Our studies also suggest that spontaneous resolution upon crystallization is very difficult to repeat even for species that have very similar molecular structures.

Supplementary material

Figures S1-S3 give the mass spectra for three complexes. Figure S4 displays the displacements from the 24-atom core plane for [Cu(ENTPP)]. CCDC 921908, 921909, and 921910 contain the supplementary crystallographic data. These data can be obtained free

of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or by application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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