Notes

Structure and Properties of Macrocyclic Nickel(II) Coordination Polymer Bearing 1,1'-Ferrocenedicarboxylate Bridging Ligand

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Ferrocene, ferrocenyl-containing ligands and functionalized ferrocenes have been widely studied not only understanding their structures, bonding and reactivities but also applying in catalytic, sensing, bioorganometallic, and medicinal research areas.[1-7] A 1,1'-ferrocenedicarboxylate (fdc) ligand, one of polycarboxylates, has attracted attention as building blocks for the construction of coordination polymers, as models for the inspection of torsional behaviors of ferrocenyl moieties, and as drug development for cancer treatment.[8-10] Although the fdc ligand has two carboxylate groups on the rigid cyclopentadienyl (Cp) rings, it is fairly flexible in binding to metal ions due to the possible rotation of Cp rings about the Cp-Fe-Cp axis.[11] Torsional angles between the Cp rings as well as between the carboxylate groups are varied depending on the environment of metal ions, resulting in more unpredictable metal-ligand arrangements and novel geometries during the construction of coordination polymers and/or supramolecular polymers.[4,8,12,13] Therefore, flexible ligands as building blocks in coordination polymers have been used widely to date. In our early work, we reported the effects of macrocycles to the torsional angles of Cp rings in macrocyclic zinc(II) complexes bearing ferrocenyl moieties, where the complexes with eclipsed and staggered structures between the Cp rings were isolated in the solid state, respectively.[8] Moreover, recent advances of functionalized ferrocenes as potential chemotherapeutic drugs urge researchers to secure more examples of complexes containing ferrocenyl moieties.[14-16] Thus, the structural characterization of ferrocenyl complexes are highly required for better understanding the corresponding conformation of ferrocenyl moieties as well as gaining more insights into the structure-activity relationship of ferrocene derivatives. On this account, we attempted the reaction of macrocyclic nickel(II) complex [Ni(**L**)](ClO$_4$)$_2$ with Na$_2$fdc in DMF/H$_2$O, and obtained a basic 1D coordination polymer containing the fdc bridging ligand. We herein report the synthesis,

characterization and crystal structure of $\{[Ni(\mathbf{L})(fdc)]\cdot 3H_2O\}_n$ in which the ferrocenyl rings adopt an anticlinal (eclipsed) conformation (*Scheme* 1).

The complex **1** (orange plates) was crystallized from the equimolar reaction of [Ni(**L**)](ClO$_4$)$_2$ and Na$_2$fdc in DMF/H$_2$O. As illustrated in *Figure* 1, the structure **1** exhibits a
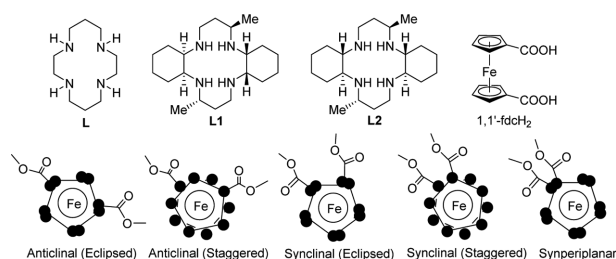
Scheme 1. Molecular structures of **L**, **L1**, **L2**, 1,1'-fdcH$_2$, and conformations of ferrocenyl rings with anticlinal (eclipsed), anticlinal (staggered), synclinal (eclipsed), synclinal (staggered), synperiplanar.
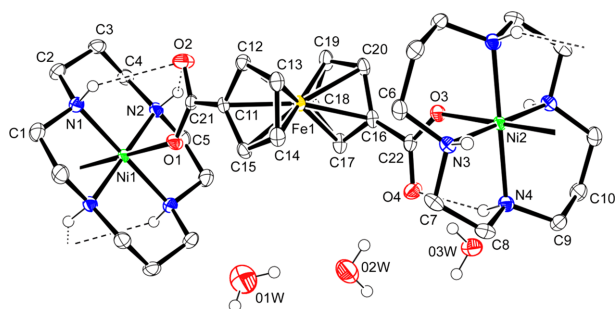
Figure 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity. Selected interatomic distances (Å) and angles (°). Ni1-N1, 2.0713(14); Ni1-N2, 2.0703(14); Ni2-N3, 2.0651(14); Ni2-N4, 2.0838(14); Ni1-O1, 2.1037(12); Ni2-O3, 2.1135(12); C21-O1, 1.260(2); C21-O2, 1.260(2); C22-O3, 1.259(2); C22-O4, 1.266(2); N1-Ni1-N2, 94.03(6); N1-Ni1-N2#1, 85.97(6); N1-Ni1-O1, 91.82(5); N1#1-Ni1-O1, 88.18(5); N2-Ni1-O1, 92.74(5); N2#1-Ni1-O1, 87.26(5); N3-Ni2-N4, 85.61(5); N3-Ni2-N4#2, 94.39(5); N3-Ni2-O3, 92.40(5); N3#2-Ni2-O3, 87.60(5); N4-Ni2-O3, 94.31(5); N4#2-Ni2-O3, 85.69(5). Symmetry codes: #1 –x+2,-y+1,-z #2 –x+1,-y,-z+1.
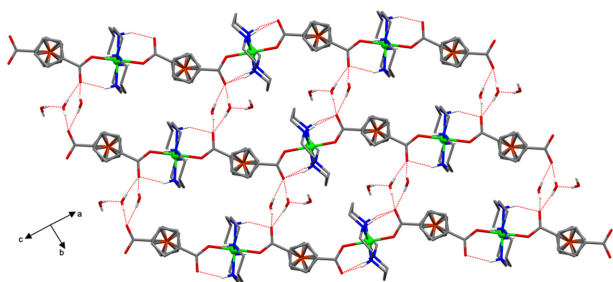
Figure 2. View of 2D structure formed with hydrogen bonding interactions between 1D chains in **1**.

Figure 3. View of two Cp rings in **1** showing anticlinal (eclipsed) conformation.

1D coordination polymer with the basic unit of [Ni(**L**)(fdc)] which is composed of nickel(II) macrocycle and bridging fdc ligand.

The fdc ligand bridges nickel(II) macrocycles to form a 1D coordination polymer in which 1D chains are connected each other by the mediation of lattice water molecules, resulting in the formation of 2D supramolecule (*Figure* 2). The nickel(II) atom sits on an inversion center and the coordination environment about the nickel(II) ion shows a distorted octahedron with four Ni-N and two Ni-O bonds. The Ni-N distances of 2.0713(14) Å, 2.0703(14) Å, 2.0651(14) Å, 2.0838(14) Å are typical for those found in octahedral nickel(II) ions. The Ni-N distances in nickel(II) macrocycles follow a general trend that shows a weaker Ni-N interaction (Ni-N = 2.07–2.10 Å) in an octahedral nickel(II) environment, while a stronger Ni-N interaction (Ni-N = 1.88–1.91 Å) is involved in a square planar nickel(II) environment.[17–19] The Ni-O distances of 2.1037(12) Å, 2.1135(12) Å are normal for such a geometry in carboxylato nickel(II) macrocycles.[20–22] The macrocyclic ligand skeleton in **1** takes the most stable *trans III*(*R,R,S,S*) configuration.[23,24] Each pair of N-H group is pre-organized, pointing to opposite direction, respectively. The Ni-O bonds are supported by intramolecular hydrogen bonds between the pre-organized N-H groups and the oxygen atoms of the carboxylates of bridging fdc ligands (N1-H1···O2: d(D···A) = 3.257(2) Å, ∠(DHA) = 130.6°; N2-H2···O2: d(D···A) = 3.157(2) Å, ∠(DHA) = 134.9°; N4-H4···O4: d(D···A) = 2.9559(19) Å, ∠(DHA) = 145.7°, *Figure* 1).

One of the carboxylate groups (C21-O1 and C21-O2) is involved in bifurcating hydrogen bonding with a pair of N-H groups (N1-H1 and N2-H2), but the other is not. Two Cp rings of the bridging fdc ligand in **1** adopt an approximately eclipsed (anticlinal) conformation (0°; fully eclipsed, 36°; fully staggered[25]) in which the torsion angle of two Cp rings is 12.63° {measured by C12-Cp (centroid)-Cp (centroid)-C19} (*Figure* 3). The torsion angle of Cp rings in **1**
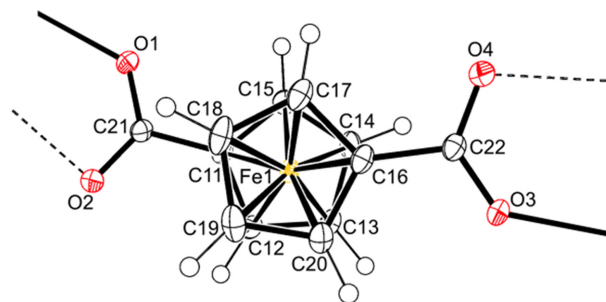
is comparable to those found in previous macrocyclic zinc(II) systems, {[Zn(**L1**)(fdc)]·3H₂O}ₙ and {[Zn(**L2**)(fdc)]·2H₂O}ₙ. The torsion angles of 24.6° in {[Zn(**L1**)(fdc)]·3H₂O}ₙ and 7.2° in {[Zn(**L2**)(fdc)]·2H₂O}ₙ were reported.[8]

The macrocycle **L1** containing two *cis*-fused cyclohexane rings on the macrocycle **L** is more steric demand, leading to an anticlinal (staggered) conformation of two Cp rings in {[Zn(**L1**)(fdc)]·3H₂O}ₙ. Whereas the less steric demand macrocycle **L2** in which has two *trans*-fused cyclohexane rings on **L** affords an anticlinal (eclipsed) conformation. The torsion angle of 12.63° in the present complex **1** is close to that found in {[Zn(**L2**)(fdc)]·2H₂O}ₙ (7.2°), indicating that the steric demand of **L** in **1** resembles **L2** rather than **L1** (*Scheme* 1). The crystal structures of 1,1'-disubstituted ferrocene derivatives or the fdc ligands which are coordinated to metal ions without macrocycles show very small torsion angles (0.1° ~ 0.9°).[4,9,12,13,15] In those cases, the relationship between the two 1,1'-substituents on Cp rings prefers to take a synclinal conformation. Even synperiplanar conformation is observed in some cases, where two Cp rings and substituents are eclipsed (*Scheme* 1).[4,26] In addition to the steric factor to the torsion angle, it is believed that the interactions between the 1D chains by the mediation of lattice water molecules could be an another factor which affects the conformation of the Cp rings of bridging fdc ligands. Since the rotational barrier of the Cp rings in ferrocene vapor has been estimated at *ca.* 0.9 ~ 1.1 kcal/mol,[27,28] the different orientation of Cp rings may not significantly affect the overall stability of **1**. Therefore, it is in principle feasible to stabilize the eclipsed conformation of two Cp rings of bridging fdc ligands by intermolecular interactions. The versatile hydrogen bonding modes in the crystalline state are believed in assisting the formation of the thermodynamically less stable eclipsed conformation of two Cp rings in **1**.

In agreement with the structure determined by X-ray diffraction methods, the broad band at 3308 cm⁻¹ in the IR

spectrum indicates the O-H stretching of lattice water molecules. The weak band at 3167 cm^{-1} was assignable to N-H stretching of the macrocycle. The strong absorptions at 1551 cm^{-1} (ν_{as}COO), 1378 cm^{-1} (ν_sCOO) were observable due to fdc ligand.[8,12,13] The solid state electronic spectrum of **1** exhibited a band maximum at 453 nm that is typical for ferrocene complexes.[29] The characteristic spectra having three band maxima expected for a d^8 nickel(II) ion in a distorted octahedral environment was not observed due to the strong absorptions of ferrocenyl moiety. The TGA curve for **1** showed a quick start of the first weight loss of 9.2% (calc. 9.2%) over ~30–280 °C, corresponding to the loss of three lattice water molecules. Further weight loss due to the loss of fdc and macrocyclic ligands was observed over ~280–360 °C range. The metallic NiO composition (obs. 12.7%, calc. 12.7%) was left at ~590 °C as a final residue.

In conclusion, we successfully synthesized and structurally characterized a new complex **1** in which the bridging fdc ligand takes eclipsed (anticlinal) conformation. The conformation of Cp rings with the torsion angle of 12.63° in **1** indicates that the steric demand by the introduction of nickel(II) macrocycle is very important in determining the extent of torsion angles as well as the conformations of ferrocenyl rings including relative positions of substituents on ferrocenyl moieties. The intermolecular interactions between the 1D coordination polymeric chains are believed to be assisting the formation of the thermodynamically less stable eclipsed conformation of two Cp rings in **1**.

EXPERIMENTAL

Materials and Measurements

All chemicals were commercially available from Aldrich and were used without further purification. Water was distilled before use for all procedures. IR spectra were recorded on a Perkin-Elmer Spectrum X spectrophotometer with Nujol mull (KBr discs) in the 4000-400 cm^{-1}. The thermal and elemental (C, H and N) analyses were performed at the analytical laboratory of KRICT, Korea. The precursor complex [Ni(**L**)](ClO$_4$)$_2$ was prepared according to the literature method.[30,31] Caution! The perchlorate salts are potentially explosive and should be handled in small quantities.

Synthesis of {[Ni(L)(fdc)]·3H$_2$O}$_n$

The complex {[Ni(**L**)(fdc)]·3H$_2$O}$_n$ (**1**) was prepared by adding an aqueous solution of Na$_2$fdc (160 mg, 0.5 mmol) to a DMF (5 mL) solution of [Ni(**L**)](ClO$_4$)$_2$ (230 mg, 0.5 mmol). The mixture was left until orange plates of **1** formed.

Table **1**. Crystal data and structure refinement for **1**

	1
Empirical formula	C$_{22}$H$_{38}$FeN$_4$O$_7$Ni
Formula weight	585.12
Temperature (K)	150 (1)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P$\bar{1}$
a (Å)	8.3828 (3)
b (Å)	9.7735 (4)
c (Å)	16.6729 (6)
α (°)	104.969 (1)
β (°)	97.666 (1)
γ (°)	102.899 (1)
V (Å^3)	1259.59 (8)
Z	2
D$_{calcd}$ (Mg/m^3)	1.543
Absorption coefficient (mm^{-1})	1.372
Independent reflections	5401 [R(int) = 0.0260]
Goodness-of-fit on F^2	1.036
Final R indices [I > 2σ(I)]	R$_1$ = 0.0256, wR$_2$ = 0.0682
R indices (all data)	R$_1$ = 0.0292, wR$_2$ = 0.0705

Suitable crystals for X-ray diffraction studies and other measurements were manually collected under a microscope. Anal. Calc. for C$_{22}$H$_{38}$FeN$_4$NiO$_7$: C, 45.16; H, 6.55; N, 9.57. Found C, 45.22; H, 6.38; N, 9.54%. IR [Nujol, cm^{-1}]: 3380 (νOH), 3167 (νNH), 1551 (ν_{as}COO), 1378 (ν_sCOO). UV/vis [BaSO$_4$; λ_{max}/nm]: 453.

X-ray Crystallography

Crystallographic data for **1** are summarized in *Table* 1. Bruker APEX2 X-ray diffractometer with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) was used for data collection. To collect sufficient data, a combination of ϕ and ω scans with κ offsets were used. The data frames were integrated and scaled using the Denzo-SMN package.[32] The structure was solved and refined, using the SHELXTL\PC V6.1 package.[33] Refinement was performed by full-matrix least squares on F^2, using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

Supplementary Materials. CCDC No. 1496630 (**1**) contains the supplementary crystallographic data. These data can

be obtained free of charge via http://www.ccdc.cam.ac.uk/ data_request/cif. Figures S1-S3 contain IR, visible spectra, and TGA curves for **1**.

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