

Supporting information

Diastereoselective self-assembly of dinuclear double- and triple-stranded helicates from a D-isomannide derivative

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Experimental part

General information. All reactions except the synthesis of **2** were performed under argon atmosphere using standard Schlenk techniques and oven-dried glassware prior to use. TLC was performed on aluminium TLC plates silica gel 60 F₂₅₄ from Merck. Detection was done by UV-light (254 and 366 nm). Products were purified by column chromatography on silica gel 60 (70–230 mesh) from Merck. ¹H and ¹³C NMR spectra were recorded on a Bruker DMX 500 spectrometer at 300 K, at 500.1 and 125.8 MHz, or a Bruker AM 400 at 298 K, at 400.1 MHz and 100.6 MHz or a Bruker Avance 300 at 298 K at 300.1 MHz and 75.5 MHz, respectively. ¹H NMR chemical shifts are reported on the δ-scale (ppm) relative to residual non-deuterated solvent as internal standard. ¹³C NMR chemical shifts are reported on the δ-scale (ppm) relative to deuterated solvent as internal standard. Signals were assigned on the basis of ¹H, ¹³C, HMQC, and HMBC NMR experiments. Mass spectra were taken on a Finnigan MAT 212 with data system MMS–ICIS (EI, CI, *iso*-butane, NH₃) or an A.E.I. MS-50 (EI; HiRes-EI). ESI-MS spectra were recorded on a Bruker APEX IV FT mass spectrometer. CD spectra were recorded on a Jasco J-810 spectro photometer using silica cells from Hellma (1 cm). Optical rotations were recorded using a Jasco P-1020 and a 10-cm-cell. Mps were measured with a hot-stage microscope SM-Lux from Leitz and are not corrected. Elemental analyses were carried out with a Fisons Instrument EA1108 or a Heraeus Vario EL. Unfortunately, fluorine containing samples cannot be analysed with these. Thus, no elemental analyses of the complexes were performed because we employed tetrafluoroborate salts in most cases to prepare the helicates. Molecular modelling studies were carried out with Spartan Pro (Wavefunction). The geometry optimizations of the cationic dinuclear metal coordination complexes were performed on a semi-empirical level of theory without taking into account the counter ions or the solvent (mixture). Most solvents were dried, distilled and stored under argon according to standard procedures. All chemicals were used as received from commercial sources. **2** (2,2'-bipyridine-5-carboxylic acid) was prepared from methyl 2,2'-bipyridine-5-carboxylate, which was prepared according to a published procedure.¹

2,2'-Bipyridine-5-carboxylic acid (**2**)

600 mg (2.80 mmol) of methyl 2,2'-bipyridine-5-carboxylate were suspended in 10 mL of THF, 1.5 mL of methanol und 6 mL of aq. NaOH (2N) and stirred for 2 h at r.t. and 16 h at

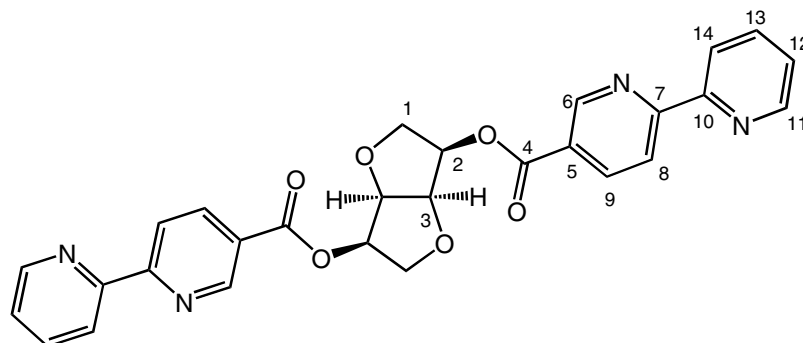
¹ Kiehne, U; Bunzen, J.; Staats, H.; Lützen, A. *Synthesis* **2007**, 1061.

reflux. The solvents were evaporated and water was added (5 mL). The resulting solution was acidified with hydrochloric acid (conc.). Precipitation of the product started immediately. After 48 h at +4 °C, the precipitate was collected by filtration. Yield: 560 mg (2.80 mmol, quantitative).

Analytical data were in accordance with the ones published.²

2,5-Bis([2,2']bipyridinyl-5-carboxyloxy)-1,4:3,6-dianhydro-D-mannitol (3)

300 mg (1.50 mmol, 2.4 equiv.) of 2,2'-bipyridine-5-carboxylic acid (**2**) were suspended in 15 mL of thionyl chloride and the resulting suspension was refluxed for 16 h. After around 2 h, **2** was completely dissolved. Thionyl chloride was removed in vacuo and the remaining solid was dried in vacuo for 5 h. CH₂Cl₂ (15 mL) was added to dissolve the product 2,2'-bipyridine-5-carbonyl chloride (**8**). 91 mg (0.62 mmol) of carefully dried D-isomannide (**1**) were dissolved in 10 mL of CH₂Cl₂, 3 mL of Et₃N, and 5 mL of pyridine and the resulting solution was added dropwise to the dissolved carbonyl chloride at r.t.. (It is important to notice that **1** has to be dried in vacuo for at least 18 h prior to use due to its extremely hygroscopic properties). After refluxing for 16 h, the reaction mixture was cooled down and filtrated over celite. The filter was rinsed with CH₂Cl₂ (100 mL), the filtrate washed with water (7x 100 mL) and the aq. layers was extracted with CH₂Cl₂ and dried with Na₂SO₄. The solvents were evaporated and the crude product was purified by column chromatography (ethyl acetate + 5 % Et₃N, R_f = 0.51). Yield: 200 mg (0.39 mmol, 63 %), mp 170-172 °C.



¹H -NMR (δ [ppm], 500.1 MHz, CDCl₃): 4.06-4.11 (m, 2 H, H-1) , 4.17-4.21 (m, 2 H, H-1') , 4.94(d, 2 H, H-3, ³J = 4.4 Hz), 5.41 (d, 2 H, H-2, ³J = 5.5 Hz), 7.39 (ddd, 2 H, H-12, ³J_{11,12} = 3.8 Hz, ³J_{12,13} = 6.6 Hz, ⁴J not resolved), 7.88 (ddd, 2 H, H-13, ³J_{12,13} = 6.6 Hz, ³J_{13,14} = 7.7 Hz, ⁴J not resolved), 8.48 (dd, 2 H, H-9, ³J_{8,9} = 8.2 Hz, ⁴J_{5,9} = 1.6 Hz), 8.52 (d, 2 H, H-14, ³J_{13,14} = 7.7 Hz), 8.57 (d, 2 H, H-8, ³J_{8,9} = 8.2 Hz), 8.73 (d, 2 H, H-11, ³J_{11,12} = 3.8 Hz), 9.34 (s, 2 H, H-6)

¹³C-NMR (δ [ppm], 125.8 MHz, CDCl₃): 70.7 (C-1), 74.5 (C-2), 80.7 (C-3), 120.7 (C-8), 122.2 (C-14), 124.7 (C-12), 125.1 (C-5), 137.5 (C-13), 138.3 (C-9), 149.1 (C-11), 150.7 (C-6), 154.2 (C-10), 159.1 (C-7), 164.7 (C-4)

² Ghadiri, M. R.; Soares, C.; Choi, C. *J. Am. Chem. Soc.* **1992**, *114*, 825.

CD (CH₂Cl₂/CH₃CN (9:1) [λ ($\Delta\epsilon$): 301 nm (+45)

[α]_D²⁰: +311.8 ° (c = 0.50, CH₂Cl₂)

MS (EI) m/z (%) 510.2 ([C₂₈H₂₂N₄O₆]⁺, 100)

HR-MS (EI) calc.: 510.1539, found: 510.1541

Anal. calc. for C₂₈H₂₂N₄O₆·0.2 H₂O: C 65.42 %, H 4.39 %, N 10.90 %. Found C 65.48 %, H 4.51 %, N 10.88 %

Preparation of the metal complexes

Ligand **3** was dissolved in CD₂Cl₂ (2 mL) and [Ag(CH₃CN)₂]BF₄, [Cu(CH₃CN)₄]BF₄, [Zn(BF₄)₂]·6.5 H₂O, or [Fe(BF₄)₂]·6 H₂O, respectively, were dissolved in CD₃CN (1 mL). Equimolar amounts of the two solutions (600 μ L of the ligand, 200 μ L of the metal salt) were combined (except in case of [Fe(BF₄)₂]·6 H₂O a 3:2 mixture of **3** and the metal salt was applied) and analyzed by ¹H- and ¹³C-NMR spectroscopic methods. Diluted solutions (CH₂Cl₂) of the complexes were analyzed by ESI MS methods afterwards.

Characterization of the metal complexes of **3**

Only the ¹H- and ¹³C-NMR-data of the silver(I)- and zinc(II) complexes are listed below due to relatively broad signals in case of the copper(I)- and iron(II)-complexes.

[Ag₂(**3**)₂](BF₄)₂

10.0 mg (19.6 μ mol) of **3** were dissolved in 2 mL of CD₂Cl₂ and 600 μ L (3.0 mg, 5.9 μ mol) were filled into an NMR tube. 8.1 mg (29.38 μ mol) of [Ag(CH₃CN)₂]BF₄ were dissolved in 1 mL of CD₃CN and 200 μ L (1.6 mg, 5.9 μ mol) of this solution were added to the solution of **3** in the tube. An immediate colour change from colourless to yellow could be observed upon mixing.

¹H-NMR (δ [ppm], 500.1 MHz, CD₂Cl₂/CD₃CN (3:1), reference CH₂Cl₂): 4.09 (dd, 2 H, H-1_{exo}, ²J_{1_{exo},1_{endo}} = -11.5 Hz, ³J_{1_{exo},2} = 3.8 Hz), 4.23 (d, 2 H, H-1_{endo}, ²J_{1_{exo},1_{endo}} = -11.5 Hz), 4.88 (m, 2 H, H-3), 5.44 (s, 2 H, H-2), 7.71 (ddd, 2 H, H-12, ³J_{11,12} = 4.9 Hz, ³J_{12,13} = 7.6 Hz, ⁴J not resolved), 8.15 (ddd, 2 H, H-13, ³J_{12,13} = 7.6 Hz, ³J_{13,14} = 8.2 Hz, ⁴J_{11,13} = 1.6 Hz), 8.37 (d, 2 H, H-14, ³J_{13,14} = 8.2 Hz), 8.39 (d, 2 H, H-8, ³J_{8,9} = 8.2 Hz), 8.68 (dd, 2 H, H-9, ³J_{8,9} = 8.2 Hz, ⁴J_{6,9} = 1.1 Hz), 8.85 (d, 2 H, H-11, ³J_{11,12} = 4.9 Hz), 9.29 (d, 2 H, H-6, ⁴J_{6,9} = 1.1 Hz)

¹³C-NMR (δ [ppm], 125.8 MHz, CD₂Cl₂/CD₃CN (3:1), reference CD₂Cl₂): 73.5 (C-2), 75.4 (C-1), 82.9 (C-3), 123.2 (C-8), 124.1 (C-14), 126.7 (C-12), 127.5 (C-5), 139.8 (C-13), 140.6 (C-9), 150.6 (C-6), 151.3 (C-10), 151.8 (C-11), 155.4 (C-7), 163.3 (C-4)

MS (ESI): m/z (%) 617.1 ([Ag₂**3**]⁺, 100), 1323.3 ([Ag₂**3**]⁺BF₄)⁺, 15)

CD (CH₂Cl₂/CH₃CN (9:1) [λ ($\Delta\epsilon$): 291 nm (-18), 310 nm (+64)

[α]_D²⁰: +376.8 ° (c = 0.345, CH₂Cl₂/CH₃CN (4:1))

[Zn₂(3**)₂](BF₄)₄**

10.0 mg (19.6 μmol) of **3** were dissolved in 2 mL of CD₂Cl₂ and 600 μL (3.0 mg, 5.9 μmol) were filled into an NMR tube. 10.5 mg (29.5 μmol) of [Zn(BF₄)₂]·6.5 H₂O were dissolved in 1 mL of CD₃CN and 200 μL (2.1 mg, 5.9 μmol) of this solution were added to the solution of **3** in the tube. [Zn(ClO₄)₂]·6 H₂O was used as metal salt for the ESI MS experiments.

¹H-NMR (δ [ppm], 500.1 MHz, CD₂Cl₂/CD₃CN (3:1), reference CH₂Cl₂): 4.07 (dd, 2 H, H-1_{exo}, ²J_{1_{exo},1_{endo}} = -11.6 Hz, ³J_{1_{exo},2} = 3.6 Hz), 4.21 (d, 2 H, H-1_{endo}, ²J_{1_{exo},1_{endo}} = -11.6 Hz), 4.86 (m, 2 H, H-3), 5.46 (m, 2 H, H-2), 7.87 (ddd, 2 H, H-12, ³J_{11,12} = 4.9 Hz, ³J_{12,13} = 7.8 Hz, ⁴J_{12,14} = 1.0 Hz), 8.38 (ddd, 2 H, H-13, ³J_{12,13} = 7.8 Hz, ³J_{13,14} = 8.2 Hz, ⁴J_{11,13} not resolved), 8.60 (d, 2 H, H-11, ³J_{11,12} = 4.9 Hz), 8.62 (d, 2 H, H-14, ³J_{13,14} = 8.2 Hz), 8.66 (d, 2 H, H-8, ³J_{8,9} = 8.3 Hz), 8.81 (dd, 2 H, H-9, ³J_{8,9} = 8.3 Hz, ⁴J_{6,9} = 1.9 Hz), 9.13 (d, 2 H, H-6, ⁴J_{6,9} = 1.9 Hz)

¹³C-NMR (δ [ppm], 125.8 MHz, CD₂Cl₂/CD₃CN (3:1), reference CD₂Cl₂): 73.4 (C-2), 75.5 (C-1), 82.8 (C-3), 123.3 (C-8), 124.1 (C-14), 128.4 (C-12), 129.2 (C-5), 142.5 (C-13), 142.8 (C-9), 148.1 (C-10), 149.1 (C-6, C-11), 152.0 (C-7), 162.3 (C-4)

MS (ESI): m/z (%) 287.0 ([Zn**3**]²⁺, 5), 673.0 ([Zn**3**ClO₄]⁺, 100), 1449.0([Zn₂**3**]₂(ClO₄)₃]⁺, 7)

CD (CH₂Cl₂/CH₃CN (9:1) [λ (Δε)]: 300 nm (-58), 320 nm (+198)

[α]_D²⁰: +417.3 ° (c = 0.367, CH₂Cl₂/CH₃CN (4:1))

[Cu₂(3**)₂](BF₄)₂**

10.0 mg (19.6 μmol) of **3** were dissolved in 2 mL of CD₂Cl₂ and 600 μL (3.0 mg, 5.9 μmol) were filled into an NMR tube. 9.3 mg (29.38 μmol) of [Cu(CH₃CN)₄]BF₄ were dissolved in 1 mL of CD₃CN and 200 μL (1.9 mg, 5.9 μmol) of this solution were added to solution of **3** in the tube. An immediate colour change from colourless to intensively deep blue could be observed upon mixing.

MS (ESI): m/z (%) 573.1 ([Cu**3**]⁺, 100), 1235.2 ([Cu₂**3**]₂(BF₄)⁺, 10),

CD (CH₂Cl₂/CH₃CN (9:1) [λ (Δε)]: 274 (-101), 313 (+110), 415 (-2.4), 450 (+1)

Due to the intensive deep blue color, no optical rotation could be measured because of a large extinction.

[Fe₂(3**)₃](SO₄)₂**

10.0 mg (19.6 μmol) **3** were dissolved in 2 mL of CD₂Cl₂ and 600 μL (3.0 mg, 5.9 μmol) were filled into an NMR tube. 6.6 mg (19.59 μmol) of [FeSO₄]·6.5 H₂O were dissolved in 1 mL of DMSO-*d*₆ and 200 μL (1.3 mg, 3.9 μmol) of this solution were added to the solution of **3** in the tube. An immediate colour change from colourless to intensively purple could be

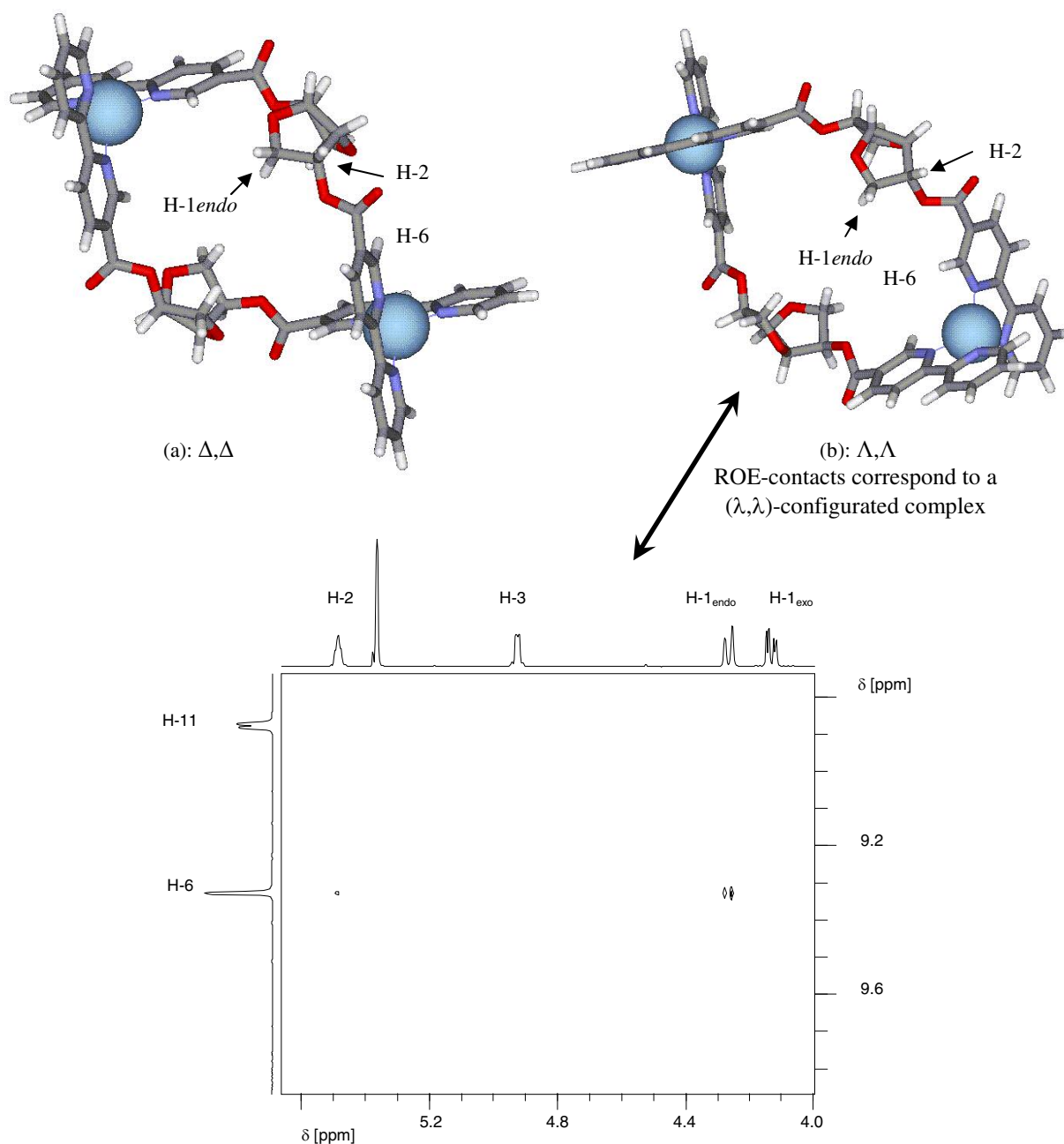
observed upon mixing. $[\text{Fe}(\text{BF}_4)_2] \cdot 6 \text{H}_2\text{O}$ was used as metal salt for the ESI MS and CD experiments.

MS (*ESI*): m/z (%): 538.4 ($[\text{Fe}_3]^{2+}$, 80), 585.1 ($\{[\text{Fe}_3]\text{F}\}^+$, 100, loss of BF_3), 908.2 ($\{[\text{Fe}_2\text{F}_3](\text{BF}_4)_2\}^{2+}$, 5)

CD ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1) $[\lambda$ ($\Delta\epsilon$): 293 nm (-187), 311 nm (+370), 351 (-7.1), 378 (+3.3), 464 (-1.6), 514 (+3.4), 583 (-7.0)

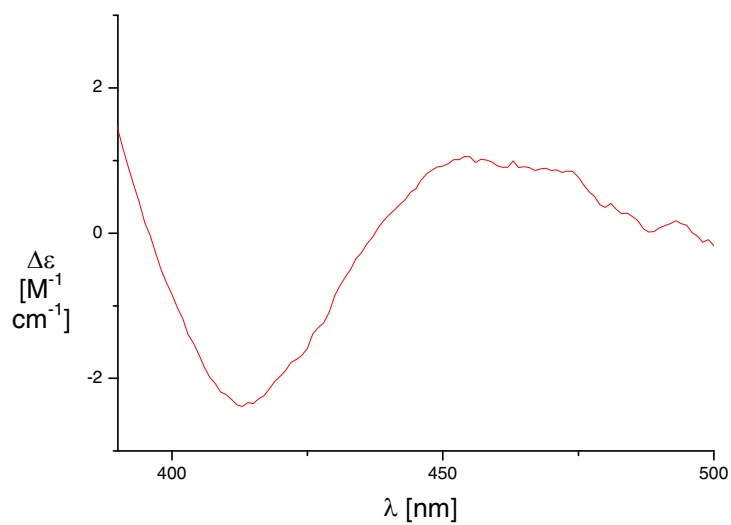
Due to the intensive purple color, no optical rotation could be measured because of a large extinction.

2D-ROESY spectrum (500.1 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ 3:1, 298 K) of $[\text{Ag}_2(3)_2](\text{BF}_4)_2$



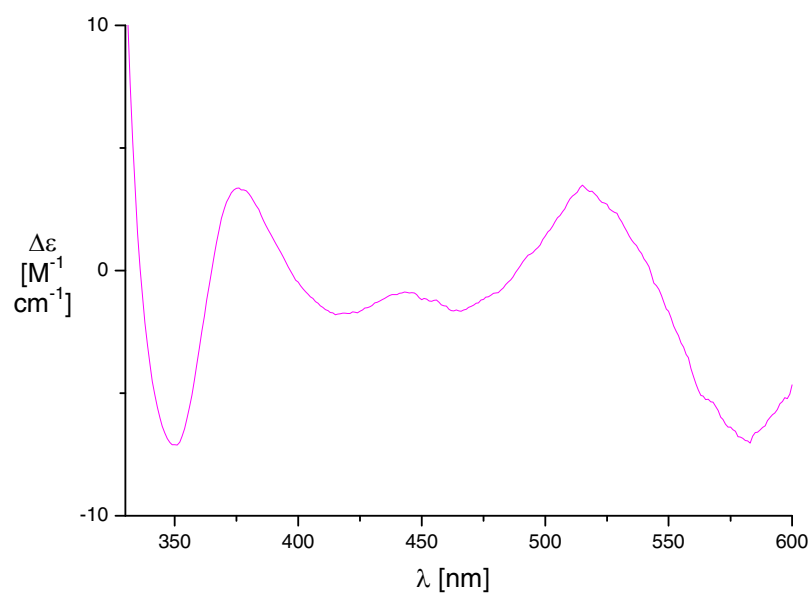
CD spectrum of $[\text{Cu}_2(\mathbf{3})_2](\text{BF}_4)_2$ (2.4×10^{-5} mol/L in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1)) :

mlct bands (400-500 nm)



CD spectrum of $[\text{Fe}_2(\mathbf{3})_3](\text{BF}_4)_2$ (1.6×10^{-5} mol/L in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1)) :

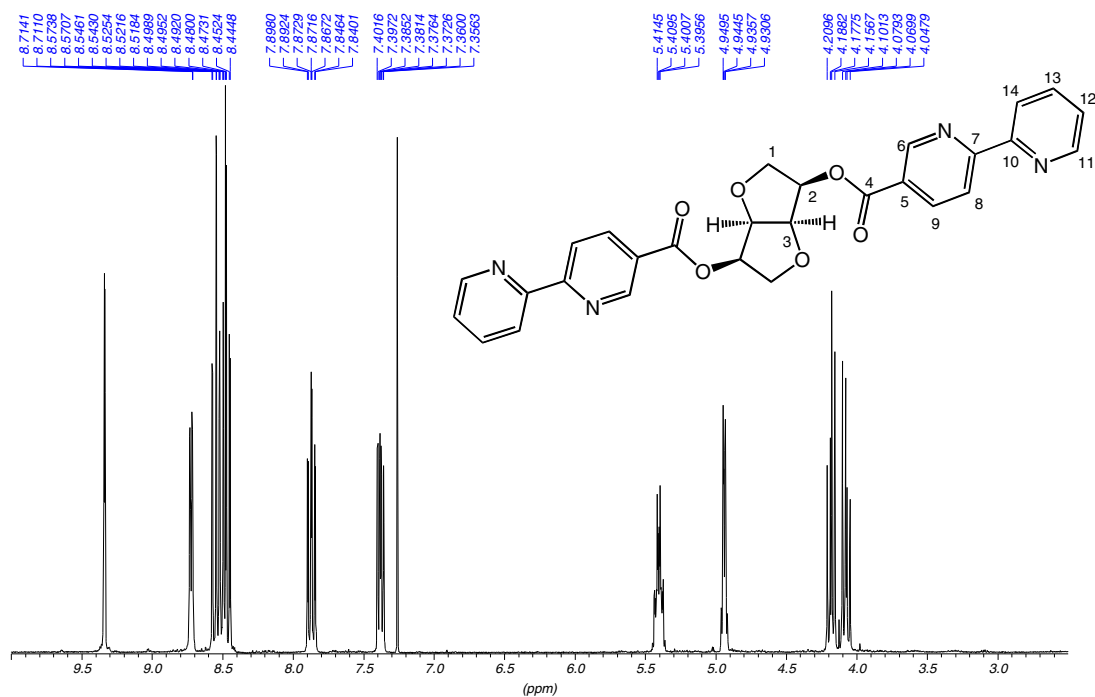
mlct bands (400-600 nm)



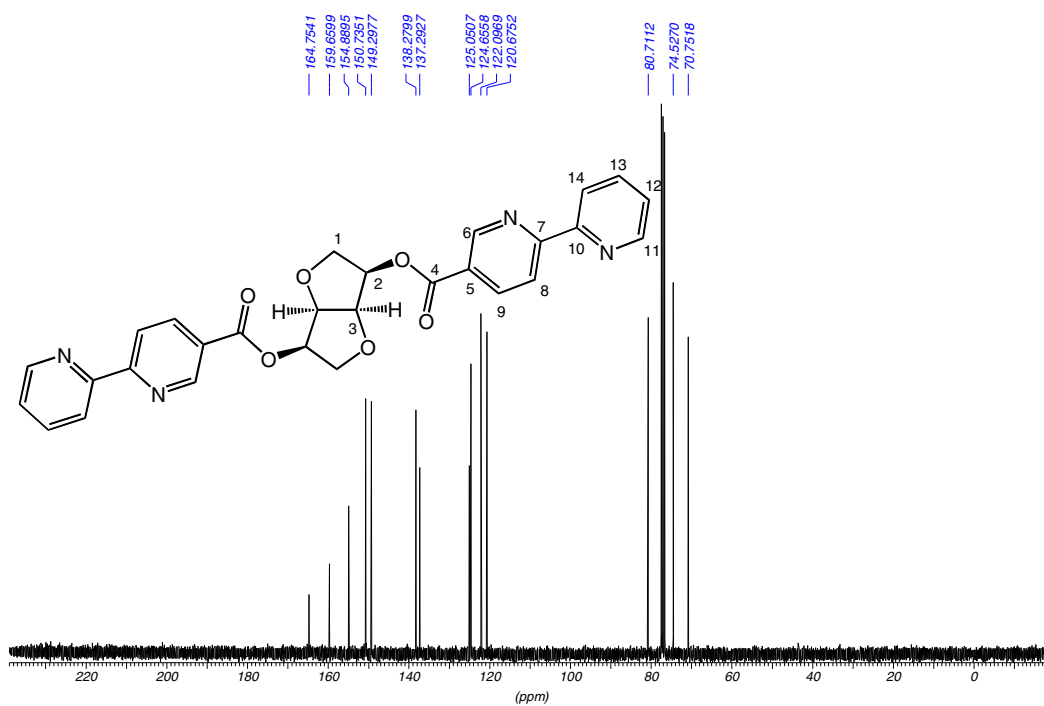
Copies of the ^1H - and ^{13}C -NMR spectra

2,5-Bis([2,2']bipyridinyl-5-carboxyloxy)-1,4:3,6-dianhydro-D-mannitol (3)

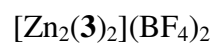
^1H -NMR (δ [ppm], 400.1 MHz, CDCl_3):



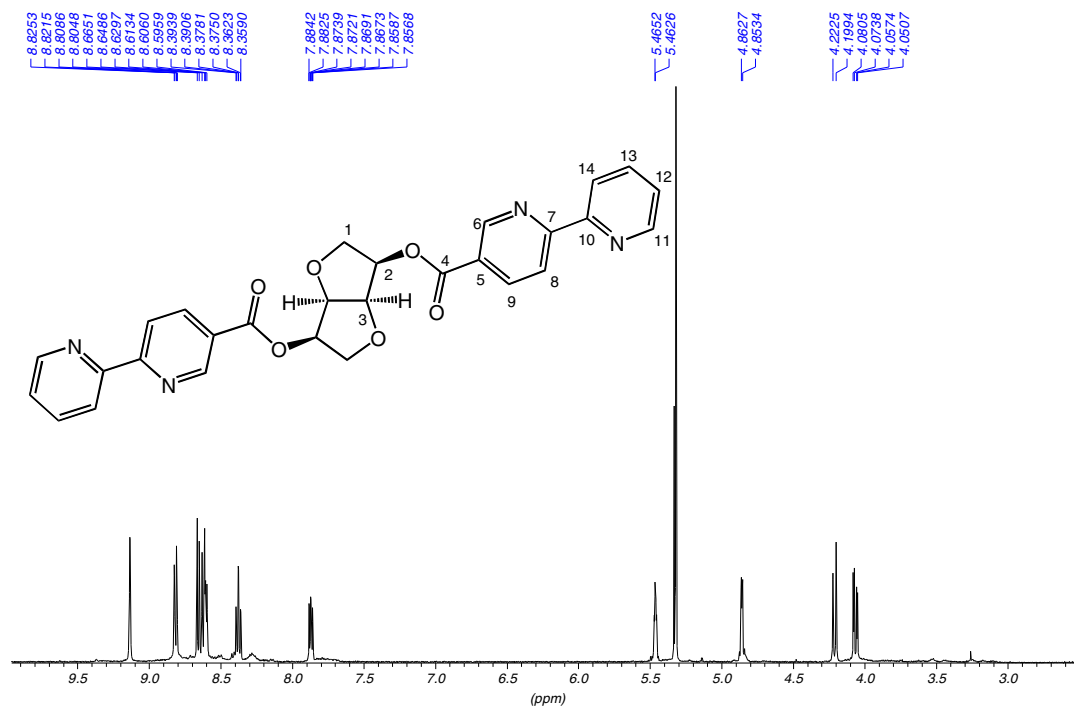
$^{13}\text{C}\{^1\text{H}\}$ -NMR (δ [ppm], 100.6 MHz, CDCl_3):



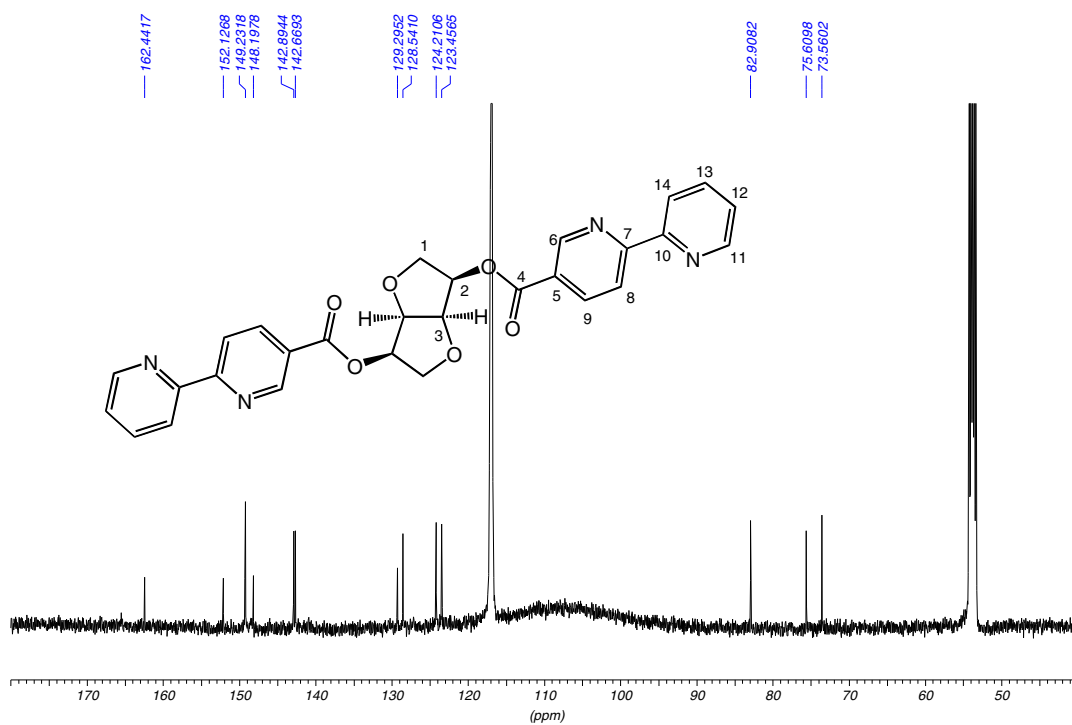
Metal complexes of 3 (only ligand structure is given)

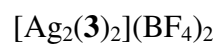


^1H -NMR (δ [ppm], 500.1 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ (3:1)):

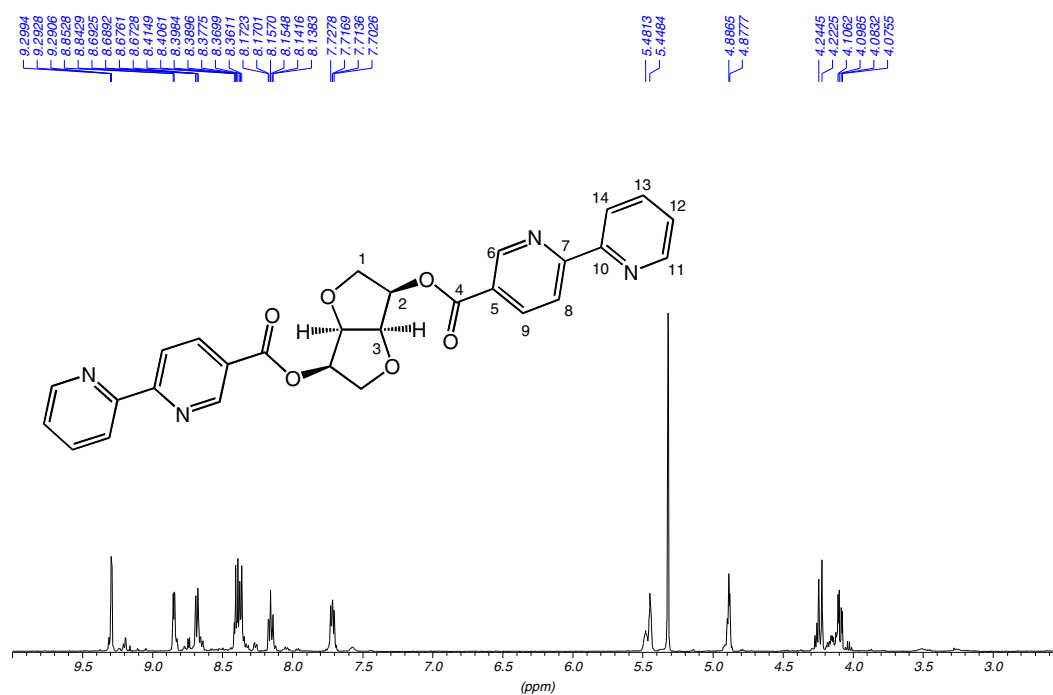


$^{13}\text{C}\{^1\text{H}\}$ -NMR (δ [ppm], 125.8 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ (3:1)):

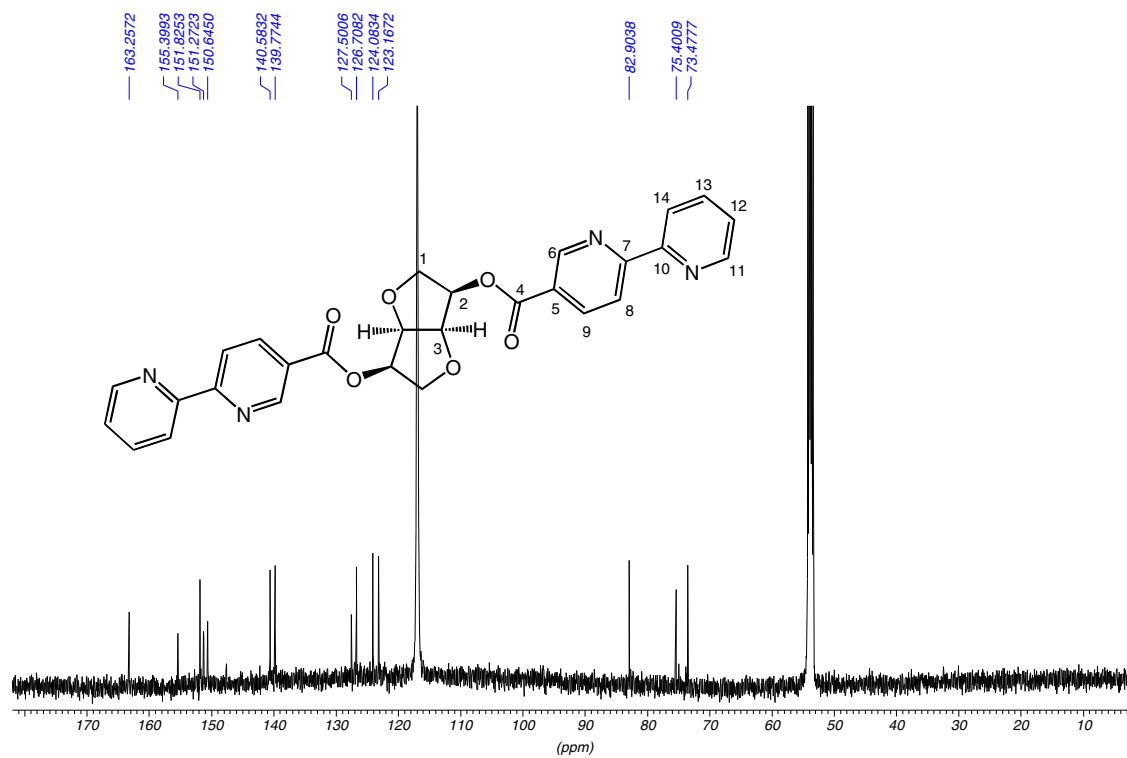


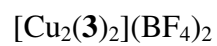


¹H-NMR (δ [ppm], 500.1 MHz, CD₂Cl₂/CD₃CN (3:1)):

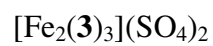
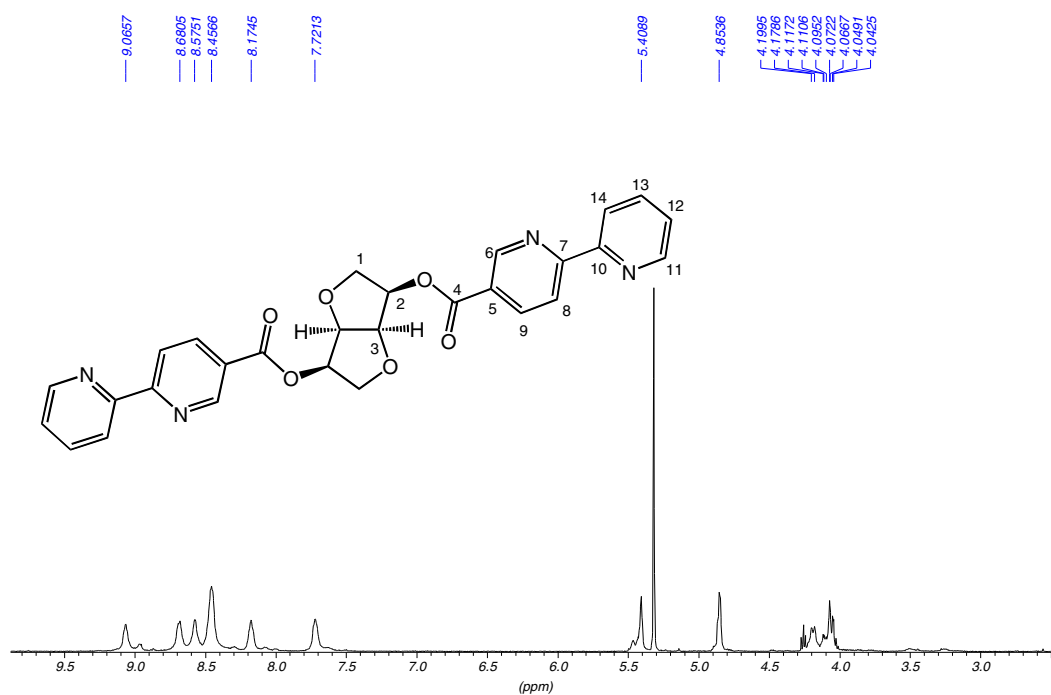


¹³C{¹H}-NMR (δ [ppm], 125.8 MHz, CD₂Cl₂/CD₃CN (3:1)):





^1H -NMR (δ [ppm], 500.1 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ (3:1)):



^1H -NMR (δ [ppm], 500.1 MHz, $\text{CD}_2\text{Cl}_2/\text{DMSO}-d_6$ (3:1)):

