Supporting Information

Stereochemistry for engineering spin crossover: structures and magnetic properties of a homochiral vs racemic [Fe(N₃O₂)(CN)₂] complex

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Table of Contents

•	S-1: Experimental	2
•	S-2: CD Spectroscopy	6
•	S-3: X-ray Crystallography	7
•	S-4: Magnetic Susceptibility Measurements	18
•	S-5: Mössbauer Spectroscopy	24
•	S-6: References	27

S-1: Experimental General

All experiments were carried out using standard Schlenk line procedures unless otherwise stated. Dry solvents were used for all experiments performed under nitrogen. Anhydrous solvents were obtained from a Puresolve PS MD-4 solvent purification system. All reagents were commercially purchased from Sigma Aldrich or Alfa Aesar. NMR spectra were recorded on a Bruker Avance AV 600 Digital NMR spectrometer with a 14.1 Tesla Ultrashield Plus magnet. Samples for IR were pressed as KBr pellets and their spectra were recorded using a ThermoMattson RS-1 FT-IR. EI and FAB mass spectra were obtained using a Kratos Concept 1S High Resolution E/B mass spectrometer. CD spectra were recorded on a Jasco J-600 spectrometer at room temperature, using J7STDANL software. Elemental analysis was carried out by Atlantic Microlab.

Synthesis of (5R,6R)-5,6-diphenyl-4,7-dioxa-1,9-decadiene (5a)

(R,R)-(+)-Hydrobenzoin (**4a**) (5.00 g, 23.3 mmol) was dissolved in THF (120 mL). Sodium hydride (1.80 g, 74.8 mmol) was added to the solution and the reaction mixture was stirred for 1 h at 30° C. A solution of allyl bromide (6.94 mL, 82.1 mmol) in THF (20 mL) was then added slowly over 30 min, after which time the reaction mixture was stirred and heated to 40° C for 2 h and then refluxed at 90° C for an additional 24 h. When no starting material remained, the reaction was allowed to cool to room temperature. A white precipitate was then removed by filtration and discarded and the filtrate was evaporated to dryness. The resulting yellow oil was dissolved in DCM (100 mL), washed with H₂O (2 x 50 mL), brine (2 x 50 mL), and dried over MgSO₄. Removal of the solvent under reduced pressure afforded (**5a**) as a pale yellow oil (4.98 g, 73%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.21 (s, 6H, 7, 8, 9-H), 7.10 (s, 4H, 6, 10-H), 5.91 (m, 2H, 2-H), 5.27 (d, *J* = 15.59 Hz, 2H, 1-H), 5.15 (d, J = 9.23 Hz, 2H, 1-H), 4.54 (s, 2H, 4-H), 4.07 (dd, *J* = 13.19 Hz, 1H, 3-H), 3.92 (dd, *J* = 13.56 Hz, 1H, 3-H); ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 138.8, 135.1, 128.1, 127.7, 127.4, 116.5, 85.1, 70.2; IR (KBr, v_{max}/cm^{-1}): 3084, 3063, 2861, 1646, 1453, 1080, 942, 701.FAB-MS *m/z* = 294 [M]⁺ (0.60%); HRMS (FAB): Found *m/z* = 294.16254 [M]⁺; Calcd. 294.16198 for C₂₀H₂₂O₂.

(4R,5R)-4,5-diphenyl-3,6-dioxa-1,8-octanediol (7a)

Compound (6) (6.48 g, 22.0 mmol) and OsO_4 (0.16 g, 0.648 mmol) in a (3:1) mixture of THF/H₂O (80 mL) were stirred in the dark, at room temperature for 4 h. NaIO₄ (27.54 g,

0.129 mol) was then added portion wise and the mixture was allowed to stir in the dark for an additional 20 h. Upon completion, the solvent was removed and the remaining product (7) was dissolved in a (1:1) mixture of DCM/MeOH (250 mL) and gravity filtered affording a pale brown solution. The solution was stirred vigorously in an ice bath during which time NaBH₄ (5.61 g, 0.148 mol) was added cautiously over a 1 h period. The reaction mixture was then stirred for an additional 19 h at room temperature. On completion, the solvent was removed, and the crude product was dissolved in H_2O (500 mL) and stirred in a beaker for 1 h. The product was extracted into DCM (3 x 300 mL) and the organic phase was washed with 1 M HCl (2 x 50 mL), water (2 x 50 mL) and brine (2 x 50 mL), and then dried over MgSO₄. The solvent was then removed under reduced pressure to afford the crude product that was purified via column chromatography on silica gel, eluting with a (20:1) mixture of CHCl₃/MeOH to give (**7a**) as a yellow oil (5.64 g, 84 %). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.21 (s, 6H, 7-H, 8-H, 9-H), 7.08 (s, 4H, 6-H, 10-H), 4.50 (s, 2H, 4-H), 3.78 (m, 4H, 3-H), 3.71 (m, 2H, 2-H), 3.52 (m, 2H, 2-H), 3.04 (s, 2H, 1-H); ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 138.3, 128.2, 127.9, 127.6, 86.9, 71.2, 61.8; IR (KBr, v_{max}/cm⁻¹): 3490, 3344, 3030, 2869, 1709, 1453, 1363, 1222, 1067; FAB-MS: m/z = 303 [MH]⁺ (7%); HRMS (FAB): Found m/z =303.15963 [M]⁺; Calcd. 303.15820 for C₁₈H₂₃O₄.

(4R,5R)-4,5-diphenyl-3,6-dioxa-1,8-octanediphthalimide (8a)

Diisopropyl azodicarboxylate (DIAD) (8.11 g, 40.1 mmol) dissolved in THF (20 mL) was added dropwise to a solution of (**7**) (5.5 g, 18.2 mmol), phthalimide (5.89 g, 40.1 mmol) and triphenylphosphine (10.52 g, 40.1 mmol) in THF (140 mL). The reaction mixture was stirred at room temperature for 4 days. Upon completion, the solvent was removed and the crude product was purified via flash SiO₂ chromatography by first eluting with a (2:1) mixture of hexane/ ethyl acetate and then re-dissolving the product in DCM and purification second column eluting with a (3:1) mixture of petroleum ether/ethyl acetate, (R_f = 0.42). Removal of the solvent afforded (**8a**) as a white solid (3.77 g, 37 %) Mp.180-182°C; ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.84 (s, 4H, 12-H, 15-H), 7.74 (s, 4H, 13-H, 14-H), 6.94 (m, 6H, 6-H, 7-H, 8-H), 6.83 (d, J = 7.54 Hz, 4H, 5-H, 9-H), 4.41 (s, 2H, 3-H), 3.78 (dt, *J* = 15, 4.95 Hz, 4H, 2-H), 3.61 (t, *J* = 5.65 Hz, 4H, 1-H); ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 168.5, 137.9, 134.1, 133.2, 127.8, 123.2, 85.7, 66.2, 37.7; FAB-MS: *m/z* = 561 [M+H]⁺ (7 %); IR (KBr, v_{max}/cm⁻¹): 3032, 2887, 1774, 1720, 1396, 1105, 1026, 711; HRMS (FAB): Found *m/z* = 561.19623 [M]⁺;

Calcd. 561.20256 for $C_{34}H_{29}N_2O_6$; CHN: Elemental Analysis (%): Calcd. for $(C_{34}H_{28}N_2O_6)\cdot 0.5H_2O$ C: 71.69; H: 5.13; N: 4.92. Found C: 71.65, H: 5.24, N: 4.84.

Synthesis of (4R,5R)-4,5-diphenyl-3,6-dioxa-1,8-octanediamine (2a)

Hydrazine monohydrate (3.46 g, 6.90 mmol) was added to a suspension of (4R,5R)-4,5diphenyl-3,6-dioxa-1,8-octanediphthalimide¹ (3.87 g, 6.90 mmol) in warm ethanol (95 %, 200 mL), and the reaction mixture was refluxed for 28 h. On completion, the mixture was cooled to room temperature and a white precipitate was removed by gravity filtration. The precipitate was washed with cold ethanol (2 x 3 mL) and cold DCM (2 x 3 mL). The filtrate was then collected and evaporated under reduced pressure. The resulting residue was dissolved in DCM (300 mL), and washed with 2N HCl (3 x 150 mL). The aqueous phase was collected and the pH was adjusted to 10 by the addition of a 20% solution of NaOH. The mixture was then stirred for 30 minutes, and the product was extracted into DCM (3 x 60 mL), washed with H_2O (2 x 50 mL), brine (2 x 50 mL), and then dried over Na_2SO_4 . The solvent was removed to afford (2a) as a pale yellow oil (1.60 g, 78 %). αD^{20} – 7.478 (c 0.115, CHCl₃); FAB-MS: $m/z = 301 [M+H]^+ (27.1 \%)$; IR (KBr, cm⁻¹): 3364, 3294, 3030, 2921, 2866, 1453, 1265, 1102, 701; ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.19 (m, 6H, 6-H, 7-H, 8-H), 7.11 (m, 4H, 5-H, 9-H), 4.44 (s, 2H, 3-H), 3.46 (dt, *J* = 9.52, 4.85 Hz, 2H, 2-H), 3.35 (dt, *J* = 9.52, 4.85 Hz, 2H, 2-H), 2.82, (t, J = 5.23 Hz, 4H, 1-H), 2.20 (s, 4H, NH); ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 139.0, 127.8, 127.5, 86.0, 71.9, 41.9; Elemental Analysis (%): Calcd. for (C₁₈H₂₆N₂O₃) C: 67.90; H: 8.23; N: 8.80. Found C: 68.39, H: 8.04, N: 8.34.

Synthesis of (45,55)-4,5-diphenyl-3,6-dioxa-1,8-octanediamine (2b)

The [*S*,*S*]-diamine (**2b**) was prepared as described for the (*R*,*R*)-enantiomer (**2a**). All yields and data for (**2b**) and its intermediates are identical with those reported for the (*R*,*R*)-enantiomer above; αD^{20} + 7.452 (c 0.114, CHCl₃).

Synthesis of chiral Schiff-base macrocycles [Fe(dpN₃O₂)(CN)₂]·2CH₃CN·Et₂O (3a) and (3b)

2,6-Diacetylpyridine (**3**) (0.136 g, 0.833 mmol) and $Na_2S_2O_4$ (0.099 g, 0.569 mmol) in degassed H₂O (8 mL) was added to a solution of FeCl₂·4H₂O (0.166 g, 0.833 mmol) and (**2**) (0.25 g, 0.833 mmol) in degassed MeOH (10 mL). The reaction mixture was refluxed gently for 12 h and then filtered into a solution of NaCN (0.81 g, 16.4 mmol) containing $Na_2S_2O_4$ (0.048 g, 0.276 mmol) in degassed H₂O (5 mL). The product was collected by filtration, washed with H₂O (15 mL), a (1:1) mixture of Et₂O/THF (6 mL), and Et₂O (5 x 5 mL). Both

complexes were isolated as dark blue solids and recrystallized via the addition of Et_2O to a methanol solution of the complex (0.24 g, 54 % yield). IR (KBr, v_{max}/cm^{-1}): 3420, 2096, 1634, 1454, 1082, 1059, 704; MS FAB: m/z = 509 [M-CN]⁺, 100 %; Elemental Analysis (%): Calcd. for ($C_{29}H_{29}N_5O_2Fe$)·2CH₃CN·Et₂O C: 64.60; H: 6.08; N: 9.10. Found C: 64.80, H: 5.81, N: 9.23.

Synthesis of racemic Schiff-base macrocycle Fe(dpN₃O₂)(CN)₂]·2CH₃CN·Et₂O (3c)

The racemic complex 4c was prepared from a (1:1) racemic mixture of diamines (2a) and 2b, following the synthetic procedure described above for complexes (3a) and (3b). After recrystallization from CH₃CN/Et₂O, the macrocyclic complex was isolated as a blue solid in 56 % yield. IR (KBr, v_{max}/cm^{-1}): 3421, 2903, 2093, 1629, 1454, 1316, 1132, 1081, 703; MS FAB: m/z =509 [M-CN]+, (100 %); Elemental Analysis (%): Calcd. for Calcd. for (C₂₉H₂₉N₅O₂Fe)·2CH₃CN·Et₂O C: 64.60; H: 6.08; N: 9.10. Found C: 64.72, H: 5.93, N: 9.20.

S-2: CD Spectroscopy



Figure 1: Circular dichroism (CD) spectra of the R,R-[Fe(dpN₃O₂)(CN)₂] (**3a**), red line, *S*,*S*-[Fe(dpN₃O₂)(CN)₂] (**3b**), blue line and racemic [Fe(dpN₃O₂)(CN)₂] (**3c**), yellow dashed line in ethanol at room temperature.

The chirality of (**3a**) and (**3b**) was probed by circular dichroism (CD) spectroscopy, Figure 1. As expected, the CD spectrum of (**3a**) is complementary to that recorded for its S,Senantiomer (**3b**). Both enantiomers exhibit a Cotton effect, where the absorption passes through zero at approximately 340 nm, followed by a continuation in the opposite direction. The racemic complex (**3c**) displays no CD spectrum (yellow dashed line).

S-3: X-ray Crystallography

Single crystal

A single crystal of (**3a**) was suspended in paraffin oil and mounted quickly onto a nylon loop on a copper pin and flash cooled to 250 K in the stream of liquid nitrogen on the diffractometer. Once the dataset was collected, the crystal was slowly cooled at a rate of (60 K h⁻¹) to 100 K and a second low temperature dataset was collected. Data were measured using graphite-monochromated Mo-K_{α} radiation (λ = 0.71073 Å) and the APEX-II software.¹ Final cell constants were determined from full least squares refinement of all observed reflections. The data were corrected for absorption (SADABS).² For all compounds, the structures were solved by direct methods with SHELXS³ and refined by full-matrix leastsquares on F² with SHELXL-2013 in the Bruker SHELXTL suite.¹ Hydrogen atoms were placed in calculated positions and refined as riding atoms using default parameters. The Flack parameters are 0.144(23) at 250 K and 0.090(16) at 100 K indicating that they are either unreliable for this complex, or that there is a small amount of racemic twinning in the single crystal. Both the room and low temperature crystal structures of (**3a**) have been deposited with the Cambridge structural database and are assigned the codes: CCDC 1025310-1025311.

	250 K	100 K
Chemical formula	C ₆₆ H ₇₄ Fe ₂ N ₁₂ O ₅	C ₆₆ H ₇₄ Fe ₂ N ₁₂ O ₅
Formula Mass	1227.07	1227.07
Crystal system	Monoclinic	Monoclinic
a/Å	14.3466(19)	14.1310(16)
b/Å	10.7143(12)	10.5819(10)
<i>c</i> /Å	21.144(3)	20.876(2)
α/°	90	90
<i>в</i> /°	100.195(4)	99.233(4)
γ/°	90	90
Unit cell volume/ų	3198.8(7)	3081.2(6)
Temperature/K	250(2)	100(2)
Space group	P2 ₁	P21
No. of formula units per unit cell, Z	2	2
No. of reflections measured	36907	21761
No. of independent reflections	12208	11269
R _{int}	0.0791	0.1091
Final R_1 values ($l > 2\sigma(l)$)	0.0761	0.0686
Final $wR(F^2)$ values ($l > 2\sigma(l)$)	0.1557	0.1550
Final R ₁ values (all data)	0.1100	0.1229
Final wR(F ²) values (all data)	0.1758	0.1960
Absolute structure parameter	0.144 (12)	0.090 (16)

 Table 1. Summary of crystallographic data for (3a) at 250 and 100 K.

Fe1—N1	1.869 (6)	C11—C12	1.507 (13)
Fe1—N3	1.957 (7)	C11—C18	1.518 (12)
Fe1—C30	1.984 (10)	C12—C17	1.382 (13)
Fe1—C29	1.994 (10)	C12—C13	1.427 (14)
Fe1—N2	2.036 (8)	C13—C14	1.370 (15)
Fe1—02	2.261 (6)	C14—C15	1.354 (16)
Fe2—N6	2.036 (6)	C15—C16	1.351 (15)
Fe2—C58	2.097 (11)	C16—C17	1.386 (13)
Fe2—C59	2.104 (12)	C18—C19	1.512 (11)
Fe2—N8	2.125 (7)	C19—C24	1.379 (12)
Fe2—N7	2.137 (7)	C19—C20	1.394 (12)
N1—C2	1.356 (11)	C20—C21	1.399 (14)
N1—C6	1.360 (11)	C21—C22	1.354 (17)
N2—C7	1.274 (13)	C22—C23	1.395 (16)
N2—C9	1.510 (13)	C23—C24	1.380 (12)
N3—C27	1.303 (11)	C25—C26	1.493 (12)
N3—C26	1.449 (11)	C27—C28	1.491 (13)
N4—C30	1.136 (12)	C31—C32	1.382 (12)
N5—C29	1.149 (12)	C31—C56	1.490 (13)
N6—C35	1.335 (11)	C32—C33	1.392 (13)
N6-C31	1.357 (11)	C33—C34	1.384 (13)
N7—C56	1.280 (11)	C34—C35	1.390 (11)
N7—C55	1.488 (12)	C35—C36	1.489 (12)
N8—C36	1.284 (11)	C36—C37	1.514 (12)
N8—C38	1.468 (11)	C38—C39	1.518 (13)
N9—C59	1.130 (14)	C40—C41	1.505 (12)
N10-C58	1.113 (13)	C40—C47	1.553 (11)
N12—C66	1.279 (17)	C41—C42	1.366 (13)
N13—C60	1.104 (14)	C41—C46	1.398 (12)
01—C10	1.420 (13)	C42—C43	1.402 (14)
01—C11	1.462 (11)	C43—C44	1.396 (16)
02—C25	1.439 (9)	C44—C45	1.340 (17)
O2—C18	1.449 (9)	C45—C46	1.387 (13)
O3—C54	1.424 (9)	C47—C48	1.514 (12)
O3—C47	1.436 (10)	C48—C49	1.377 (13)
O4—C40	1.429 (10)	C48—C53	1.378 (13)
O4—C39	1.433 (10)	C49—C50	1.389 (14)
O5—C63	1.421 (14)	C50—C51	1.380 (16)
O5—C64	1.468 (14)	C51—C52	1.350 (18)
C2—C3	1.392 (12)	C52—C53	1.405 (15)
C2—C27	1.475 (13)	C54—C55	1.517 (12)
C3—C4	1.385 (15)	C56—C57	1.496 (12)

Table 2. Selected bond lengths (Å) for (3a) at 250 K.

1.378 (15)	C60-C61	1.428 (16)
1.387 (14)	C62—C63	1.509 (15)
1.484 (14)	C64—C65	1.417 (15)
1.508 (13)	C66—C67	1.281 (17)
1.480 (15)		
	1.378 (15) 1.387 (14) 1.484 (14) 1.508 (13) 1.480 (15)	1.378 (15) C60—C61 1.387 (14) C62—C63 1.484 (14) C64—C65 1.508 (13) C66—C67 1.480 (15) C60—C61

Table 3. Selected angles ($^\circ)$ for (3a) at 250 K.

N1—Fe1—N3	79.8 (3)	C7—N2—Fe1	115.1 (7)
N1—Fe1—C30	94.5 (4)	C9—N2—Fe1	120.7 (7)
N3—Fe1—C30	95.3 (4)	C27—N3—C26	123.3 (8)
N1—Fe1—C29	94.5 (3)	C27—N3—Fe1	118.2 (6)
N3—Fe1—C29	90.4 (3)	C26—N3—Fe1	118.3 (6)
C30—Fe1—C29	170.1 (4)	C35—N6—C31	120.1 (7)
N1—Fe1—N2	79.7 (4)	C35—N6—Fe2	120.2 (6)
N3—Fe1—N2	159.4 (3)	C31—N6—Fe2	119.7 (6)
C30—Fe1—N2	88.5 (3)	C56—N7—C55	121.8 (8)
C29—Fe1—N2	89.0 (3)	C56—N7—Fe2	118.5 (6)
N1—Fe1—O2	157.3 (3)	C55—N7—Fe2	119.7 (6)
N3—Fe1—O2	77.5 (3)	C36—N8—C38	121.5 (8)
C30—Fe1—O2	87.7 (3)	C36—N8—Fe2	118.9 (6)
C29—Fe1—O2	85.6 (3)	C38—N8—Fe2	119.5 (6)
N2—Fe1—O2	123.0 (3)	C10-01-C11	115.2 (8)
N6—Fe2—C58	92.4 (3)	C25-02-C18	112.7 (6)
N6—Fe2—C59	98.0 (3)	C25—O2—Fe1	105.2 (5)
C58—Fe2—C59	169.6 (4)	C18—O2—Fe1	130.0 (5)
N6—Fe2—N8	74.5 (3)	C54—O3—C47	114.7 (6)
C58—Fe2—N8	90.4 (4)	C40—O4—C39	114.3 (6)
C59—Fe2—N8	93.2 (3)	C63-05-C64	105.4 (10)
N6—Fe2—N7	74.9 (3)	N1-C2-C3	120.4 (9)
C58—Fe2—N7	90.2 (3)	N1-C2-C27	111.9 (7)
C59—Fe2—N7	91.6 (3)	C3—C2—C27	127.7 (9)
N8—Fe2—N7	149.4 (3)	C4—C3—C2	118.9 (10)
C2-N1-C6	121.7 (7)	C5-C4-C3	119.2 (9)
C2—N1—Fe1	118.7 (6)	C4—C5—C6	121.4 (10)
C6—N1—Fe1	119.5 (6)	N1-C6-C5	118.2 (10)
C7—N2—C9	123.9 (9)	N1-C6-C7	110.9 (8)

Table 4. Selected bond lengths (Å) for (3a) at 100 K.

Fe1—N1	1.831 (7)	C11-C12	1.513 (14)
Fe1—N3	1.918 (8)	C11—C18	1.518 (14)
Fe1—C29	1.940 (11)	C12—C13	1.387 (13)

Fe1—C30	1.944 (12)	C12—C17	1.389 (14)
Fe1—N2	2.026 (9)	C13—C14	1.362 (14)
Fe1—02	2.250 (7)	C14—C15	1.388 (14)
Fe2—N6	1.857 (7)	C15—C16	1.378 (14)
Fe2—C58	1.977 (12)	C16—C17	1.400 (14)
Fe2—C59	1.981 (13)	C18—C19	1.511 (13)
Fe2—N8	2.015 (8)	C19—C20	1.384 (14)
Fe2—N7	2.016 (8)	C19—C24	1.393 (14)
N1-C6	1.348 (13)	C20-C21	1.385 (13)
N1-C2	1.355 (12)	C21-C22	1.403 (15)
N2—C7	1.303 (13)	C22—C23	1.378 (16)
N2—C9	1.482 (13)	C23—C24	1.391 (15)
N3—C27	1.316 (12)	C25-C26	1.532 (13)
N3-C26	1.423 (13)	C27—C28	1.507 (14)
N4-C30	1.160 (14)	C31—C32	1.403 (13)
N5—C29	1.163 (13)	C31—C56	1.481 (14)
N13-C60	1.138 (14)	C32—C33	1.395 (14)
N6-C35	1.342 (13)	C33—C34	1.378 (14)
N6-C31	1.370 (12)	C34—C35	1.415 (14)
N7—C56	1.296 (12)	C35—C36	1.456 (14)
N7—C55	1.464 (13)	C36—C37	1.517 (14)
N8-C36	1.280 (12)	C38—C39	1.496 (14)
N8—C38	1.472 (13)	C40-C41	1.502 (13)
N9—C59	1.143 (15)	C40—C47	1.532 (13)
N10-C58	1.159 (14)	C41—C46	1.397 (14)
N12-C66	1.110 (13)	C41—C42	1.395 (15)
01—C11	1.424 (11)	C42—C43	1.371 (15)
O1-C10	1.424 (12)	C43—C44	1.388 (16)
O2—C18	1.438 (11)	C44—C45	1.393 (16)
O2 —C25	1.445 (12)	C45—C46	1.390 (14)
O3—C47	1.425 (11)	C47—C48	1.516 (14)
O3—C54	1.432 (11)	C48—C49	1.377 (14)
O4—C40	1.405 (11)	C48—C53	1.383 (15)
O4—C39	1.442 (11)	C49—C50	1.371 (15)
O5—C63	1.429 (12)	C50-C51	1.399 (18)
O5—C64	1.448 (13)	C51—C52	1.395 (17)
C2—C3	1.405 (13)	C52—C53	1.378 (16)
C2—C27	1.444 (14)	C54—C55	1.527 (14)
C3—C4	1.400 (14)	C56—C57	1.504 (14)
C4—C5	1.382 (14)	C60-C61	1.466 (15)
C5—C6	1.376 (14)	C62—C63	1.519 (13)
C6—C7	1.462 (14)	C64—C65	1.480 (16)
С7—С8	1.476 (14)	C66—C67	1.458 (14)

C9—C10	1.521 (14)	
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N1—Fe1—N3	81.5 (4)	C14-C13-C12	121.5 (10)
N1—Fe1—C29	94.0 (4)	C13-C14-C15	119.4 (10)
N3—Fe1—C29	90.8 (4)	C16-C15-C14	120.6 (10)
N1—Fe1—C30	94.4 (4)	C15-C16-C17	119.7 (9)
N3—Fe1—C30	95.1 (4)	C12-C17-C16	119.6 (9)
C29—Fe1—C30	170.4 (4)	O2-C18-C19	110.5 (8)
N1—Fe1—N2	80.4 (4)	02-C18-C11	107.2 (8)
N3—Fe1—N2	161.8 (3)	C19-C18-C11	111.2 (8)
C29—Fe1—N2	88.6 (4)	C20-C19-C24	119.7 (9)
C30—Fe1—N2	88.2 (4)	C20-C19-C18	120.8 (9)
N1—Fe1—O2	160.0 (3)	C24-C19-C18	119.3 (9)
N3—Fe1—O2	78.5 (3)	C19-C20-C21	120.4 (10)
C29—Fe1—O2	86.5 (4)	C20-C21-C22	118.9 (10)
C30—Fe1—O2	87.2 (4)	C23-C22-C21	121.7 (10)
N2—Fe1—O2	119.6 (3)	C22-C23-C24	118.3 (11)
N6—Fe2—C58	93.5 (4)	C23-C24-C19	121.1 (11)
N6—Fe2—C59	99.6 (4)	O2-C25-C26	106.8 (8)
C58—Fe2—C59	166.9 (4)	N3-C26-C25	107.7 (8)
N6—Fe2—N8	78.8 (3)	N3-C27-C2	112.1 (9)
C58—Fe2—N8	89.9 (4)	N3-C27-C28	125.2 (10)
C59—Fe2—N8	92.9 (4)	C2—C27—C28	122.6 (8)
N6—Fe2—N7	80.0 (3)	N5-C29-Fe1	178.1 (10)
C58—Fe2—N7	90.5 (4)	N4—C30—Fe1	175.3 (10)
C59—Fe2—N7	91.4 (4)	N6-C31-C32	121.7 (9)
N8—Fe2—N7	158.8 (3)	N6-C31-C56	111.3 (8)
C6-N1-C2	122.0 (8)	C32—C31—C56	127.0 (9)
C6—N1—Fe1	120.0 (7)	C33-C32-C31	116.8 (9)
C2—N1—Fe1	117.9 (7)	C34—C33—C32	122.4 (9)
C7—N2—C9	121.4 (9)	C33—C34—C35	117.5 (10)
C7—N2—Fe1	113.6 (7)	N6-C35-C34	121.6 (9)
C9—N2—Fe1	124.3 (7)	N6-C35-C36	111.0 (8)
C27—N3—C26	123.4 (9)	C34—C35—C36	127.4 (10)
C27—N3—Fe1	116.5 (7)	N8-C36-C35	114.1 (9)
C26—N3—Fe1	120.0 (6)	N8-C36-C37	126.8 (9)
C35—N6—C31	120.0 (8)	C35—C36—C37	119.1 (9)
C35—N6—Fe2	120.5 (6)	N8-C38-C39	110.8 (9)
C31—N6—Fe2	119.5 (7)	O4—C39—C38	106.4 (8)
C56—N7—C55	118.8 (9)	O4-C40-C41	113.7 (9)
C56—N7—Fe2	115.8 (7)	O4—C40—C47	104.6 (7)

 Table 5. Selected bond angles (°) for (3a) at 100 K.

C55—N7—Fe2	125.4 (6)	C41—C40—C47	111.5 (7)
C36—N8—C38	120.7 (9)	C46-C41-C42	118.4 (10)
C36—N8—Fe2	115.7 (7)	C46-C41-C40	120.9 (9)
C38—N8—Fe2	123.4 (6)	C42-C41-C40	120.6 (10)
C11-01-C10	114.7 (8)	C43-C42-C41	120.4 (10)
C18—O2—C25	111.1 (7)	C42—C43—C44	120.5 (11)
C18—O2—Fe1	132.9 (6)	C45—C44—C43	120.7 (10)
C25—O2—Fe1	104.6 (5)	C44—C45—C46	118.0 (11)
C47—O3—C54	114.4 (7)	C45-C46-C41	121.9 (11)
C40—O4—C39	114.2 (7)	O3—C47—C48	112.8 (8)
C63—O5—C64	110.7 (9)	O3-C47-C40	103.4 (7)
N1-C2-C3	120.0 (9)	C48—C47—C40	112.7 (8)
N1-C2-C27	112.0 (8)	C49—C48—C53	118.9 (10)
C3—C2—C27	128.0 (9)	C49—C48—C47	121.6 (10)
C4—C3—C2	118.1 (10)	C53—C48—C47	119.3 (10)
C5—C4—C3	119.8 (9)	C50—C49—C48	122.0 (11)
C6-C5-C4	120.4 (10)	C49—C50—C51	118.3 (11)
N1-C6-C5	119.7 (9)	C50-C51-C52	120.8 (11)
N1-C6-C7	111.6 (8)	C53—C52—C51	118.7 (11)
C5—C6—C7	128.6 (9)	C52—C53—C48	121.2 (11)
N2-C7-C6	114.2 (9)	O3-C54-C55	105.4 (8)
N2-C7-C8	127.8 (10)	N7-C55-C54	109.3 (9)
C6—C7—C8	118.0 (9)	N7-C56-C31	113.3 (9)
N2-C9-C10	110.3 (9)	N7—C56—C57	125.1 (9)
O1-C10-C9	114.5 (8)	C31—C56—C57	121.5 (9)
O1-C11-C12	111.2 (8)	N10-C58-Fe2	178.4 (10)
O1-C11-C18	103.4 (8)	N9—C59—Fe2	175.5 (11)
C12-C11-C18	113.7 (8)	N13-C60-C61	179.3 (15)
C13-C12-C17	119.2 (9)	O5-C63-C62	110.2 (9)
C13-C12-C11	120.7 (9)	O5—C64—C65	108.5 (11)
C17-C12-C11	120.0 (9)	N12-C66-C67	178.5 (17)

Table 6. Unit cell data comparison for (3a) and (3b) at 150 K.

Complex	R,R – (3a) (full data)	S,S, - (4b) (unit cell)
Crystal system	monoclinic P	monoclinic P
a/Å	14.1310(16)	14.12
b/Å	10.5819(10)	10.50
c/Å	20.876(2)	20.75
α/°	90	90
β/°	99.233(4)	99.48
γ/°	90	90
Unit cell volume/Å ³	3081.2(6)	3036
Temperature/K	100(2)	100

Shape analysis of (4a)



Figure 2. CSM for macrocycles A and B at 250 K.

The coordination geometries of macrocycles **A** and **B** were examined further by calculating the continuous shape measures (CSMs) for various 6- and 7-coordinate idealized polyhedra. The calculations reveal that molecule **A** is best described as 6-coordinate, but the large CSM value of 3.06 confirms that the octahedron is significantly distorted visible in Figure 2 (left), where the coordination sphere of the macrocycle is superimposed on an ideal octahedron. In contrast, molecule **B** is very close to being ideal D_{5h} symmetry, reflected in the small CSM value of 0.33, (Figure, 2, right).

Crystal packing of (3a)

Figure 3 shows the crystal packing of macrocycle (**3a**) at 250 K, which crystallizes together with two independent CH_3CN molecules and one Et_2O molecule. Examination of the crystal packing shows that the closest intermolecular distance between Fe^{II} centres is 10.541(2) Å. A view down the *c*-axis of the unit cell reveals that the macrocycles pack in an offset head-

to-tail arrangement. There are no significant π - π interactions between the pyridine rings of neighbouring macrocycles which is likely due to the bulky nature of the phenyl rings. The solvent molecules occupy the voids in the structure. There are no classical hydrogen bonds present in the complex; the hydrogen bonding interactions at both 100 and 250 K are summarized in Table 3. As expected the H-bonds are longer in the structure measured at 250 K and three interactions are lost upon warming. In contrast to Nelson's parent macrocycle (**1**) there are no short intermolecular H-bonding interactions involving the ether oxygen atoms of the N₃O₂ macrocycle since at both temperatures these oxygen atoms are involved in an intramolecular H-bond to the hydrogen atom of a phenyl ring. In addition there is no significant change in the framework of the H-bonding interactions between the two temperatures and all of these interactions are long giving rise to weak cooperativity in the crystal lattice.



Figure 3. Crystal packing of (3a) at 250 K showing the H-bonds as green dashed lines.

Table 7. H-bonding interactions in the crystal structure of (3a) at 100 and 250 K

	100 K			250 K		
Contact	Distance H …A (Å)	Distance D…A (Å)	D-H···A(°)	Distance H…A (Å)	Distance D…A (Å)	D-H…A (°)
C(4)H(4)···N(12)	2.58	3.477(15)	162	-	-	-
C(5) -H(5) -N(10)	2.46	3.477(15)	153	2.51	3.389(15)	158
C(14)H(14)····N(10)	2.55	3.445(15)	161	2.61	3.505(16)	162
C(21)H(21)····O(5)	2.47	3.361(13	159	2.57	3.462(14)	160
C(21)H(21)N(5)	2.54	3.461(14)	169	2.56	3.473(15)	166
C(32)H(32)····N(4)	2.52	3.437(13)	170	2.57	3.494(12)	170
C(38)H(38A)…N(9)	2.53	3.281(15)	134	2.53	3.276(14)	134
C(57)H(57B)····N(4)	2.58	3.522(15)	167	-	-	-
C(61)H(61A)····N(5)	2.34	3.221(16)	152	-	-	-

Powder XRD - Powder X-ray diffraction experiments were undertaken on a Bruker D8 Discover powder diffractometer equipped with a Hi-Star detector and GADDS software package. Data for **3a** and **3c** were collected in the range 4 < 20 < 28°, and were recorded in 0.05° steps using Cu-K_{α} radiation (λ = 1.54187 Å) with the tube operating at 40 kV and 40 mA with an initial beam diameter of 0.5 mm. Variable temperature data were collected on (**3c**) on cooling from 20 °C to -173 °C and then on warming back up to 20 °C

Powder XRD for (**3a**) collected at 250 K was compared with the simulated data for (**3a**) from single crystal measurements collected at 250 K to confirm that the microcrystalline solid and the single crystals were isostructural.



Figure 4. PXRD data for (**3a**) (blue) collected at 250 K *vs* similated powder pattern from single crystal data (orange) collected at 250 K.



Figure 5. VT PXRD data for (3c) on cooling from 20°C to -173°C and then on warming back to 20°C.

S-4: Magnetic Susceptibility Measurements Variable temperature measurements Complex (3a)

A polycrystalline sample of (**3a**) was introduced into the SQUID magnetometer at 300 K and the magnetic susceptibility was recorded on slow cooling from 300 to 10 K in 3 K steps. Care was taken not to freeze in the LS state by flash cooling the sample. The magnetic susceptibility was further recorded in warming mode from 10 to 300 K in 3 K steps. The magnetic properties in the high temperature region (280 to 370 K) were recorded in one cycle starting at 280 K warming up to 370 K and then cooling back to 280 K in 3 K steps, Figure 6. At 370 K, the $\chi_M T$ value is 2.78 cm³Kmol⁻¹ which is less than the expected value of 3.3 cm³Kmol⁻¹ for a 100 % HS Fe^{II} complex with a g value of 2.10 indicating that the SCO transition is incomplete. Decreasing the temperature leads to a continuous and very smooth decrease in $\chi_M T$ down to 50 K at where it reaches the value 0.64 cm³Kmol⁻¹. Between 50 and 25 K, $\chi_M T$ remains roughly constant, whereas it decreases again below 25 K to reach the value of 0.43 cm³Kmol⁻¹ at 10 K. Increasing the temperature shows that no thermal hysteresis is present.



Figure 6: Temperature dependence of the $\chi_M T$ product for (**3a**). The red crosshairs represent the temperature at which the $\chi_M T$ product is consistent with a 1:1 mixture of HS and LS complex.

The spin transition is very gradual, with incomplete conversion at low (10 K) and high temperature (370) K. The small decrease in $\chi_M T$ below 25 K can be attributed to the zero field splitting of the remaining high spin fraction. At approximately 240 K the complex is

comprised of 50 % HS and 50 % LS complex (red crosshairs, Figure 6). The very gradual nature of the spin transition can possibly be traced back to the absence of any strong cooperativity between molecules and/or a distribution of molecular environments. A thermal quenching of the high spin state was attempted by cooling the sample very rapidly from room temperature to 10 K, but the high spin fraction at 10 K was the same as that obtained via slow cooling; suggesting that thermal quenching of the high spin state is not feasible for this compound.

Complex (3c)

A plot of χ MT *vs* T for (**3c**) is shown in Figure 7. Taking a mean value of 3.0 cm³ K mol⁻¹ for the expected χ *M*T value for the pure HS state, the HS fraction can be estimated to be only about 23 % at low temperature which increases only very slightly to 32 % at 350 K. This indicates that the majority of the complex is in the low spin S= 0 state and does not undergo a spin transition in the solid state.



Figure 7. A plot of χM T vs T for (**3c**).

LIESST measurements Complex (3a) Reflectivity studies

The chiral complex (**3a**) was first studied by diffuse reflectance. The measurement was conducted in the visible region as a function of temperature between 280 K and 10 K. Two figures, as the result, are shown below to verify the existence of Light Induced Spin State Trapping (LIESST) in this sample. We firstly elucidated the evolution of total reflectivity upon varying the temperature, Figure 8. The total reflectivity diminishes continuously from room temperature to about 150 K, and then remains essentially constant until 75 K, whereas below 75 K it increases significantly. The decrease in reflectivity between 280 K and 150 K is classically attributed to thermal spin transition and the increase at low temperature is attributed to a LIESST effect. Magnetic measurements were performed in order to clarify this assumption.



Figure 8: Total reflectivity of complex (3a) as a function of temperature.

It can be seen that the reflectivity curves recorded in cooling and warming modes are essentially identical, that is to say that the complex does not present enough cooperativity between the Fe^{II} centers to exhibit a LITH effect visible in the reflectivity curve.

We secondly illustrate the evolution of absorption spectra at certain wavelength upon varying the temperature. This evolution indicates the capability of the complex to undergo a photoconversion, Figure 9.



Figure 9. Absorption of (**3a**) as a function of wavelength for different temperatures. Left: High temperature range (280 K to 100K), right: Low temperature range (100 K to 10 K).

In order to choose the appropriate wavelength of irradiation for the SQUID measurement, the diffuse reflectivity spectra as a function of wavelength were plotted at different temperatures. Indeed, the wave length of irradiation should normally be chosen so that the absorption of the low-spin state is higher that the absorption of high-spin state, in order to favor the LIESST effect as compared to the reverse-LIESST effect. The left plot in figure 9 shows the absorption between room temperature (HS complex) and 100 K (low spin complex). Thus the low spin compound absorb more than the high spin compound below 620 nm, whereas the reverse is true for wavelength higher than 620 nm. For photomagnetic measurements, it seems logical to irradiate at wavelength lower than 620 nm. Between 100 K and 10 K, the reverse tendency is observed: for example, the formation of a photo-induced high-spin state at low temperature under the continuous irradiation of the reflectivity. Concerning now the attribution of the various bands, at high wavelength, the absorption band reasonably belongs to a *d-d* transition the high spin state of the compound. The absorption band in the 500-620 nm is reasonably linked to the *d-d* or MLCT band of the LS state.

2. Magnetic measurements.

Attempts to photo-excite the (R,R) complex (**3a**) in the SQUID cavity with light of different wavelengths were performed. The best photomagnetic conversion was obtained by illuminating the

sample with green light (λ = 514 nm) at 10 K. After the compound was photoexcited for 10 hours with a power source of 70 mW at the entry of the glass fiber, the light was switched off. And $\chi_M T$ reached a value of 0.86 cm³Kmol⁻¹, compared with 0.43 cm³Kmol⁻¹ before irradiation. In order to approximate the temperature at which the photoexcited spin state relaxes, the temperature was continuously increased in the dark at 0.3 Kmin⁻¹ and the magnetization recorded in 1 K steps. The χ_{M} T plot is almost constant up to 40 K, when it decreases slightly and remains more or less constant up to 125 K, the temperature at which the curve merges with the thermal spin transition recorded in the dark, (Figure 6, open circles). It should be emphasized that the photoconversion of this complex is small and very far from being complete. If we estimate the value as a percentage of the conversion observed between 10 and 370 K, where the $\chi_M T$ values are respectively of 0.43 and 2.78 $cm^{3}Kmol^{-1}$, the photoconversion is about (0.86-0.43)/ (2.78-0.43) = 18.3 %. This is in sharp contrast to the photo-induced conversion of the parent $[Fe(N_3O_2)(CN)_2]$ complex 1 that was complete at 10 K.⁴ Accurately defining a T_(LIESST) for such a low conversion is difficult. Possibly, the very slow decrease of $\chi_M T$ with increasing temperature is a consequence of a larger energy barrier to lattice reorganization for this complex since the structural rearrangements taking place in the crystal lattice could hindered by the bulky nature of the phenyl substituents on the macrocyclic ring. However, it remains clear that this complex displays a modest LIESST effect which is the first time such a photoconversion from LS to HS has been observed for an enantiomerically pure Fe^{II} spin crossover complex with ligand centered chirality.

Complex (3c)

Reflectivity studies

Photoexcitation measurements were also performed on (**3c**) by applying a thin layer of the powder on an adhesive tape. The experiment was carried out between 280 and 10K with 2 cycles. The behavior of the total reflectivity over the two cycles is identical. There is a slight change of state between 280 K and 75 K, and then from 75 K to 10 K the state is changed back, Figure 10. However, it should be emphasized that the changes in reflectivity with temperature are much smaller than for complex (**3a**) and as a consequence, no LIESST effect is expected for this complex.



2. Magnetic susceptibility studies

Photo irradiation experiments were performed as shown in Table 7. No photo-induced high spin Fe^{II} complex was observed in the SQUID.

Temperature	Wavelength	Power	Time	Observation
10 K	514.5 nm	65 mW/cm	20 mins	No change
3 K	514.5 nm	215 mW/cm	20 mins	No change
10 K	647.1 nm	65 mW/cm	4 hrs	No change
3 K	647.1 nm	120 mW/cm	20 mins	No change
10 K	I.R.	35 mW/cm	20 mins	No change

Table 8. Summary of photo irradiation experiments for (3c).

S-5: Mössbauer Spectroscopy

Mössbauer spectra were recorded with a constant-acceleration spectrometer (Wissel GMBH, Germany) in a horizontal transmission mode using a 50 mCi ⁵⁷Co source . A Janis SHI-850-1 closed cycle helium refrigerator cryostat was used for variable temperature measurements. All spectra were fitted by Lorentzian line shapes using NORMOS (Wissel GMBH) least-square fitting program. The velocity scale was normalized with respect to metallic iron at room temperature, hence all isomer shifts were recorded relative to metallic iron. The numbers in parenthesis are error bars obtained from the theoretical fittings to the experimental data. In fitting the data, quadrupole spectral components corresponding to the two different spin states of iron (HS and LS) in the materials were assumed and the theoretical fit to the experimental data (red line in the Figures) is the sum of these two sub-spectra. The isomer shifts, quadrupole splittings and peak areas were determined from the fitted sub-spectra. The fractional occupation of HS and LS sites by Fe in the materials was determined from the peak areas of the sub-spectra.

Т (К)	δ^* (mm/s)	∆E _Q (mm/s)	Fe occupancy (%)	Fe ²⁺ spin state
5	0.234(4)	1.660(5)	62	Low
	1.113(4)	3.058(7)	38	High
50	0.220(4)	1.650(7)	62	Low
	1.120(5)	3.068(8)	38	High
100	0.210(5)	1.64(6)	60	Low
	1.005(5)	3.047(8)	40	High
150	0.18(1)	1.62(2)	58	Low
	1.08(1)	2.97(2)	42	High
230	0.12(1)	1.56(2)	53	Low
	1.08(1)	2.74(3)	47	High
293	0.25(3)	0.68(3)	44	Low
	0.86(1)	2.866(9)	56	High

*The isomer shift is relative to metallic iron at 293K. Note δ is the isomer shift and ΔE_Q is the quadrupole splitting. Due to broadening of the spectrum at high temperatures, the data at 293 K is not as accurate as those at lower temperatures.



Figure 11. Percentage of HS and LS Fe^{II} sites in (**3a**) as a function of temperature determined from the Mössbauer data.

Racemic Complex (3c)

In order to more accurately determine the percentage occupancy of HS and LS Fe(II) sites in the material, Mössbauer spectra were recorded from 293 - 5 K on crystalline sample of (**3c**), Figure 12.



Figure 12: Mössbauer spectra of a microcrystalline sample of (**3c**) from 293- 5 K (red line); HS Fe(II) (green line); LS Fe(II) (blue line).

Т (К)	δ* (mm/s)	ΔE _Q (mm/s)	Fe occupancy (%)	Fe ²⁺ spin state
5	0.281(2)	1.580(4)	90.4	Low
	1.007(6)	2.93(3)	9.6	High
50	0.275(1)	1.572(3)	91	Low
	1.15(2)	2.87(3)	9	High
100	0.270(1)	1.576(3)	91	Low
	1.14(1)	2.85(3)	9	High
150	0.257(3)	1.577(5)	92.3	Low
	1.12(2)	2.93(4)	7.7	High
200	0.239(4)	1.554(7)	92	Low
	1.00(3)	2.75(6)	8	High
250	0.196(5)	1.530(9)	91	Low
	1.00(4)	2.69(9)	9	High
293	0.197(2)	1.534(5)	84	Low
	1.09(3)	2.38(6)	16	High

Table 10. Mössbauer parameters and Fe^{II} site occupancy for the racemic complex (3c)

*the isomer shift is relative to metallic iron at 293K.

Due to broadening of the spectrum at high temperatures, the data at 293 K is not as accurate as those at lower temperatures.



Figure 13. Percentage of HS and LS Fe^{II} sites in (**3c**) as a function of temperature determined from the Mössbauer data.

As observed from the data between 0 and 250 K the complex is comprised of less than 20 % HS Fe^{II} that increases slightly at 300 K.

S-6: References

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