Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic supplementary information

Bis-meridional Fe^{2+} spincrossover complexes of phenyl and pyridyl substituted 2-(pyridin-2-yl)-1,10-phenanthrolines

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Content

1 Synthesis and materials characterisation

All reactions were performed under inert argon atmosphere using standard Schlenk and cannula techniques. Elemental analysis on carbon, hydrogen and nitrogen were carried out using a Thermo FlashAE 1112 analyzer. ^{1}H NMR was recorded on a Bruker Avance III 500 spectrometer at 500.30 MHz for ^{1}H and 125.80 MHz ^{13}C. ^{1}H and ^{13}C chemical shifts are given relative to tetramethylsilane and are referenced to residual solvent protons. Mass spectra were recorded with a Bruker micrOTOF-QIIa mass spectrometer operating in ESI mode. Acetonitrile (analytical grade) was available from Acros Organics and stored over molecular sieve (4 Å). $[N^{n}Bu_4][B(C_6F_5)_4]$ was prepared by metathesis of $Li[B(C_6F_5)_4]\cdot nEt_2O$ (Boulder Scientific) with $[N^{n}Bu_4]Br$ according to a published procedure.[1] Its purification was enhanced by a filtration step of the crude product through a pad of silica using dichloromethane as a solvent. All electrochemical experiments were carried out under an atmosphere of argon in acetonitrile solutions of the analyte (≈ 5 mM), containing 0.1 mol·L^{-1} of $[N^{n}Bu_4][B(C_6F_5)_4]$ as supporting electrolyte.[2,3] A two electrode setup was used; no corrections for solution resistance and double layer capacitance were applied. The Ag electrode served as pseudo reference and no correction for a possible drift were applied. A two electrode cell, which utilised an Ag electrode formed as a pot to hold the solution (0.05 mL) and Pt working electrode (18 µm nominal diameter) was used. The whole setup was placed in a Faraday cage. The working electrode was cleaned by polishing on a Buehler MicroFloc first with 1 µm and then with 1/4 µm diamond paste. The applied potentials were referred to ferrocene which was used as internal standard.

1.1 Synthesis of ligands

1.1.1 Synthesis of 2-phenyl-9-(pyridin-2-yl)-1,10-phenanthroline (**2b**)

2-(Pyridin-2-yl)-1,10-phenanthroline[4] (0.5 g, 1.94 mmol) was dissolved in dry toluol (10 mL) and carefully transferred via cannula into a solution of PhLi (1.02 mL, 1.9 M, 1.94 mmol in dibutyl ether) in dry toluol (15 mL) at 5°C. The yellow solution was stirred overnight at 30°C and carefully quenched with water. The reaction mixture was extracted with CH_2Cl_2 and the product was oxidised using an excess of activated MnO_2 (1 g) during 2 h stirring. The solution was filtrated through celite. The solvents were reduced to obtain crude **2b** as yellow oil. The crude product was forced to crystallization by the addition of hexane to give **2b** as a grey powder (0.4 g) yield 62 %. **E.A.**: calc. for $C_{23}H_{15}N_3$; C: 82.86, H: 4.54, N: 12.60; found C: 82.75, H: 4.54 N: 11.84. **^{1}H NMR** (500.30 MHz, $CDCl_3$) δ(ppm) 9.04 (d, *J* = 7.7 Hz, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 8.69 (t, *J* = 4.8 Hz, 1H), 8.40 (d, *J* = 7.2 Hz, 2H), 8.33 (t, *J* = 8.4 Hz, 1H), 8.26 (t, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.93 (td, *J* = 7.7, 1.8 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.33 (ddd, *J* = 7.4, 4.8 Hz, 1H). **^{13}C NMR** (125.80 MHz, $CDCl_3$) δ: 156.9, 156.4, 155.9, 149.0, 146.2, 145.9, 139.6, 136.9, 136.8, 136.6, 129.4, 129.2, 128.9, 127.9, 127.7, 126.7, 126.7, 125.0, 122.4, 120.5, 120.0;

1.1.2 Synthesis of 2-(6-phenylpyridin-2-yl)-1,10-phenanthroline (**2c**)

2-(6-Bromopyridin-2-yl)-1,10-phenanthroline,[5] **2a** (0.1 g, 0.29 mmol), phenylboronic acid (0.079 g, 0.48 mmol) and $Pd(PPh_3)_4$ (0.003 g, 0.0029 mmol) were dissolved in dry toluene (20 mL) under argon atmosphere and stirred for 30 min; to the mixture, NaO^tBu (0.29 g, 2,91 mmol) was added and the solution was refluxed overnight. The reaction mixtures were extracted with CH_2Cl_2. The solvent was reduced to dryness and the obtained crude **2c** was recrystallized from mixture ethanol/water 1/1(v/v) to give **2c** as grey powder (0.06 g, 62.1 %) from **2a**. **E.A.**: calc. for $C_{23}H_{15}N_3$; C: 82.86, H: 4.54, N: 12.60; found C: 82.75, N: 11.87, H: 4.41. **^{1}H NMR** (500.30 MHz, $CDCl_3$) δ(ppm): 9.18 (dd, *J* = 4.3, 1.7 Hz, 1H), 9.00 (d, *J* = 8.4 Hz, 1H), 8.95 (dd, *J* = 7.8, 0.8 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.15 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.93 (dd, *J* = 7.8, 5.9 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.77 – 7.74 (m, 5.9 Hz, 1H), 7.60 (dt, *J* = 8.0, 4.2 Hz, 1H), 7.50 – 7.45 (t, 2H, 5.5 Hz), 7.41 – 7.35 (t, 1H, 5.2, 3.3 Hz). **^{13}C NMR** (125.80 MHz, $CDCl_3$) δ: 156.6, 156.4, 155.8, 150.3, 146.4, 145.7, 139.5, 137.7, 136.7, 136.2, 129.1, 129.0, 128.9, 128.7, 126.9, 126.6, 126.5, 122.8, 121.1, 120.7;

1.1.3 Synthesis of 2,9-di(pyridin-2-yl)-1,10-phenanthroline (**2d**)

To a cold (-80°C) freshly prepared solution of 2-lithio-pyridine (4 mmol) in THF (5 mL) was added a solution of 2-(pyridin-2-yl)-1,10-phenanthroline (600 mg, 2.3 mmol) in THF (10 mL). The solution was stirred for 30 min at -80°C then slowly warmed to -40°C and stirred for 30 min. The reaction was quenched by the addition of methanol (1 mL). To this solution was added activated MnO_2 (5 g) and the suspension was stirred overnight. To the suspension methylenchloride (30 mL) was added and the suspension was filtered through a pad of celite. The solvents were reduced to dryness. The crude material was subjected to flash column chromatography (dichloromethane). Eluted solution was reduced in volume (0.5 mL). This solution was dropwise added to stirred volume of diethyl ether (10 mL). During the addition the desired compound **2d** precipitates from the solution. The identity of the compound (150 mg, 15% yield) was confirmed by reported data.[6]

1.2 Synthesis of complexes

The synthesis of $[Fe(\mathbf{2a})_2](X)_2\cdot$has been described previously.[7] General protocol for complex synthesis: To a solution of the respective ligand **2** (0.1 mmol) in dichloromethane and ethanol (1:1 5 mL) a solution of $[Fe(H_2O)_6](BF_4)_2$ or $[Fe(H_2O)_6](ClO_4)_2$ (0.04 mmol) in ethanol (3 mL) was added. The solution turned immediately deep purple (**2b**), pale red (**2c**) or pale purple (**2d**). The solvents were reduced (to 1 mL) to aid precipitation of the complexes. The crude product was washed with small portions of ethanol and diethyl ether.

$[Fe(\mathbf{2b})_2](BF_4)_2$, yield: 60%, **E.A.**: calc. (%) for $C_{46}H_{30}B_2F_8FeN_6$; C: 61.65, H: 3.37, N: 9.38 found: C: 61.60, H:3.20, N: 9.28; **FTIR** (KBr) cm^{-1}: 3445(s), 3054(m), 1573(m), 1460(m), 1100(w), 950(w), 750(w); $E^{0'}$(*vs* Fc/Fc$^+$) = 0.80 V (Fe$^{2+/3+}$ couple); ESI-MS (CH_2Cl_2/acetonitrile): m/z calcd. for $\{[Fe(\mathbf{2b})_2](ClO_4)\}^+$: 821.1366 found 821.1388.

$[Fe(\mathbf{2c})_2](BF_4)_2$, yield: 72%, **E.A.**: calc. (%) for $C_{46}H_{30}B_2F_8FeN_6$; C: 61.65, H: 3.37,N: 9.38 found: C: 61.62, H: 3.27, N: 9.30 **FTIR** (KBr) cm^{-1}: 3442(s), 3050(m), 1575(m), 1460(m), 1110(w), 950(w), 752(w). $E^{0'}$(*vs* Fc/Fc$^+$) = 0.84 V (Fe$^{2+/3+}$ couple).

[Fe(**2d**)$_2$](ClO$_4$)$_2$·CH$_3$CN, yield: 50%, **E.A.**: calc. (%) for $C_{44}H_{28}Cl_2FeN_8O_8$·(CH$_3$CN); C: 57.28, H: 3.24, N:13.07 found: C: 57.20, H: 3.08, N: 13.00; $E^{0'}$(*vs* Fc/Fc$^+$) = 0.65 V (Fe$^{2+/3+}$ couple); ESI-MS (CH$_2$Cl$_2$/acetonitrile): m/z calcd. for (**2d**+H)$^+$: 335.1291 found 335.1304; calcd for [Fe(**2d**)$_2$]$^{2+}$: 362.0893 found 362.0919.

1.3 SQUID measurements

Magnetic susceptibility data were collected by using a Quantum Design MPMS-XL SQUID magnetometer under an applied field of 0.5 T over the temperature range 5 to 400 K in the settle mode. The samples were placed in gelatine capsules held within a plastic straw. The data were corrected for the diamagnetic magnetisation of the sample holder of the ligands by using tabulated Pascal's constants.

2 X-ray analysis

Suitable crystals of all investigated compounds were obtained by slow vapor diffusion of diethyl ether to a solution of the respective complex in acetonitrile or acetone solution.

2.1 Data recording and refinement

Diffraction data was collected on an Oxford Gemini S diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å, [Fe(**2b**)$_2$](BPh$_4$)$_2$) or Cu Kα (1.54184 Å, [Fe(**2c**)$_2$](BF$_4$)$_2$ and [Fe(**2d**)$_2$](ClO$_4$)$_2$). All structures were solved by direct methods and refined against IF_oI^2 with SHELXS-2013 and SHELXL-2013,[6,7] respectively (Table 1-SI/Table 2-SI). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed with SHELXL constraints at calculated positions with a riding model. In case of [Fe(**2d**)$_2$](ClO$_4$)$_2$ the ClO$_4^-$ anion is dynamically disordered and has been refined on two positions to split occupancies of 0.28/0.72. The acetonitrile packing solvent molecule is statistically disordered along a crystallographically imposed C_2 axes going through the atom C1A. Therefore, the asymmetric unit contains an acetonitrile packing solvent molecule with an occupation factor of 0.500.

Table 1-SI: data for crystal structure refinement.

	[Fe(**2b**)$_2$](BPh$_4$)$_2$ ·(110 K)	[Fe(**2b**)$_2$](BPh$_4$)$_2$ ·(RT)	[Fe(**2c**)$_2$](BF$_4$)$_2$ ·2((CH$_3$)$_2$CO)	[Fe(**2d**)$_2$](ClO$_4$)$_2$ ·(CH$_3$CN)
CCDC-Nr.	1549553	1549554	1549555	1549556
empirical formula	$C_{46}H_{30}FeN_6$ ·2($C_{24}H_{20}B$)	$C_{46}H_{30}FeN_6$ ·2($C_{24}H_{20}B$)	$C_{46}H_{30}FeN_6$ ·2(BF$_4$) ·2(C_3H_6O)	$C_{44}H_{28}FeN_6$ ·2(ClO$_4$) ·2(CH$_3$CN)
formula weight (g/mol)	1361.03	1361.03	1012.38	964.55
T (K)	110	270	110	120
Wavelength (Å)	0.71073	0.71073	1.54184	1.54184
crystal system	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2/n$	$Pbcn$
unit cell dimensions				
a (Å)	20.5424(3)	20.6009(6)	14.3151(5)	20.1322(7)

b (Å)	13.9845(2)	14.2939(4)	7.6008(3)	11.2883(3)
c (Å)	24.5450(4)	24.6015(7)	22.0055(9)	17.4177(6)
α (°)	90	90	90	90
β (°)	103.002(2)	103.049(3)	95.758(4)	90
γ (°)	90	90	90	80
volume	6870.39(19)	7057.3(4)	2382.25	3958.3(2)
Z	4	4	2	4
μ (cm^{-1})	0.276	0.269	3.225	4.914
F(000)	2848	2848	1040	1976
Θ-range for data coll. (°)	2.941 to 25.000	2.927 to 25.000	3.869 to 64.981	4.392 to 65.968
limiting indices	$-24 \le h \le 24$ $-16 \le k \le 15$ $-28 \le l \le 29$	$-24 \le h \le 24$ $-16 \le k \le 14$ $-29 \le l \le 29$	$-16 \le h \le 10$ $-8 \le k \le 8$ $-25 \le l \le 25$	$-18 \le h \le 23$ $-10 \le k \le 13$ $-17 \le l \le 20$
reflections coll. / unique	39824 / 9979 [R_{int} = 0.0263]	38331 / 12286 [R_{int} = 0.0378]	7260 / 4010 [R_{int} = 0.0280]	11724 / 3438 [R_{int} = 0.0576]
data / restraints / parameters	12084/916/927	12286/1011/910	4010 /0/ 321	3438/88/333
GooF on F^2	1.054	1.052	1.034	1.053
final R indices ($I > 2\sigma(I)$)	R_1 = 0.0618 wR_2 = 0.1640	R_1 = 0.0595 wR_2 = 0.1542	R_1 = 0.0610 wR_2 = 0.1599	R_1 = 0.0765 wR_2 = 0.1859
(all data)	R_1 = 0.0757 wR_2 = 0.1559	R_1 = 0.0895 wR_2 = 0.1729	R_1 = 0.0702 wR_2 = 0.1741	R_1 = 0.1112 wR_2 = 0.2075
larg. diff. peak and hole (e$^-$/Å^3)	1.536 and −1.044	0.719 and −0.619	0.899 and −0.349	1.580 and −0.740

2.2 Selected bond lengths and angles

Table 2-SI: Selected bond lengths and angles in the solid state structures of salts [Fe(**2**)$_2$](X)$_2$

	[Fe(**2b**)$_2$](BPh$_4$)$_2$ ·(110 K)	[Fe(**2b**)$_2$](BPh$_4$)$_2$ ·(RT)	[Fe(**2c**)$_2$](BF$_4$)$_2$ ·2((CH$_3$)$_2$CO)	[Fe(**2d**)$_2$](BF$_4$)$_2$ ·(CH$_3$CN)
bond lengths				
Fe-N1	2.066(3)	2.202(3)	2.242(3)	2.408(4)
Fe-N2	1.946(2)	2.054(2)	2.119(3)	2.192(4)
Fe-N3	2.139(3)	2.223(2)	2.313(3)	2.238(4)
Fe-N4	2.085(2)	2.211(2)	-	2.715(5)
Fe-N5	1.960(2)	2.053(2)	-	
Fe-N6	2.160(2)	2.239(2)	-	
angles				
N1-Fe-N4/N1‘	87.4(1)	85.76(9)	106.70(9)	95.3(1)
N2-Fe-N5/N2‘	168.8(1)	165.37(9)	168.4(1)	134.7(2)
N3-Fe-N6/N3‘	86.18(9)	88.42(9)	114.51(9)	111.5(2)
N1-Fe-N3	156.5(1)	150.52(9)	147.0(1)	142.4(2)
N1-Fe-N4‘*	-	-	-	152.8(1)$^+$

*only applicable for [Fe(**2d**)$_2$]$^{2+}$; $^+$ shorter angl-calculate (360°-152.8(1)) to compare to N1-Fe-N3

Table 3-SI: CShM (**C**ontinuous **Sh**ape **M**easure)[10–12] indices calculated for solid state structures of complexes [Fe(**2**)]$^{2+}$ for octahedral (S_{OC-6}), trigonal prismatic (S_{TP-6}) and trigonal dodecahedral (S_{DD}) reference shapes.

complex	[Fe(**2a**)$_2$]$^{2+}$ (LS)	[Fe(**2a**)$_2$]$^{2+}$ (HS)	[Fe(**2b**)$_2$]$^{2+}$ (RT)	[Fe(**2b**)$_2$]$^{2+}$ (110K)	[Fe(**2c**)$_2$]$^{2+}$	[Fe(**2d**)$_2$]$^{2+}$
CShM (S_{OC-6})	2.64	6.22	5.35	3.68	7.42	11.22
CShM (S_{TP-6})	9.98	7.86	9.06	9.62	10.19	5.16
CShM (S_{DD})						2.38
Fe-N (Å) (shortest and largest)	1.88-2.08	2.09-2.25	2.05-2.24	1.94-2.16	2.12-2.31	2.19-2.41(2.72)*

* to weakly coordinated N4

3 DFT calculations

All DFT calculations were performed using ORCA2.9.1. [13]. TZVP basis sets[14] were used throughout. The structures of the cations [Fe(**2a-d)**$_2$]$^{2+}$ were optimized in their LS and HS states using the pure functional BP86.[15,16] SCO energies were derived from single-point calculations in the BP86-optimized positions with B3LYP* which is a re-parameterized derivative of B3LYP.[17] In this derivative of B3LYP (a_0 = 0.20), the amount of exact exchange a_0 has been reduced to 0.15. Cartesian coordinates of the BP86-optimized structures of [Fe(**2a-d)**$_2$]$^{2+}$ (*LS* and *HS*) are compiled in the Tables Table 8-SI to 14-SI and pertinent metrical features are given in Table 4-SI. The SCF energies were converged to 10^{-7} Hartree in energy. Dispersion contributions were approximated using Grimme's DFT-D3 atom-pairwise dispersion corrections of the parent B3LYP functional.[18] Numerical frequency calculations revealed the stationary points to be minima on the potential surface.

Table 4-SI: Selected bond lengths and angles in the DFT-optimized [a] complexes [Fe(**2**)$_2$]$^{2+}$ (HS metrics in brackets)

	[Fe(**2a**)$_2$]$^{2+}$	[Fe(**2b**)$_2$]$^{2+}$	[Fe(**2c**)$_2$]$^{2+}$	[Fe(**2d**)$_2$]$^{2+}$
bond lengths				
Fe-N1/1'	1.995(1) (2.221(1))	2.029(1) (2.217(3))	2.002(1) (2.236(2))	2.001(2) (2.486(1))
Fe-N2/2'	1.881(1) (2.116(1))	1.881(1) (2.084(1))	1.883(1) (2.116(1))	1.883(1) (2.230(1))
Fe-N3/3'	2.049(1) (2.211(1))	1.984(1) (2.217(2))	2.026(1) (2.205(3))	2.027(1) (2.230(1))
Fe-N4/4'				>3.9 (2.486(1))-

trans-angles				
N1/1'-Fe-N3/3'	161.1	160.9	160.6	161.0
	(148.7)	(148.7)	(148.9)	(-)
N2-Fe-N2'	170.3	169.9	168.9	171.0
	(158.7)	(156.7)	(157.6)	(-)
distortion				
Σ_{cis}	82.8	82.1	83.4	90.9
	(141.8)	(156.1)	(158.4)	(-)
$S_{OC\text{-}6}$[b]	2.39	2.26	2.55	2.15
	(6.21)	(6.85)	(6.54)	(-)
N_3/N_3' [c]	89.6	89.0	87.5	89.5
	(87.7)	(77.1)	(79.7)	(89.2)

[a] Optimized in ORCA on the BP86-D3/TZVP level of theory; [b] Avnir's continuous shape measure[11]; [c] angle between best planes through Fe-N_3 and Fe-N_3.

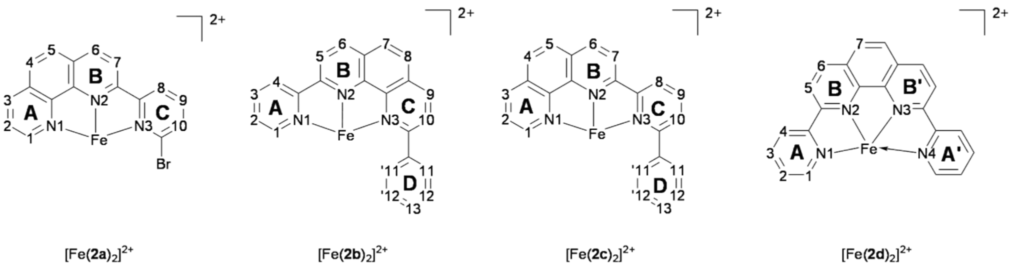
Table 5-SI: DFT-derived apparent SCO energies [a] $\Delta_{SCO}E$ [kJ /mol] of $[Fe(\mathbf{2})_2]^{2+}$

	$[Fe(\mathbf{2a})_2]^{2+}$	$[Fe(\mathbf{2b})_2]^{2+}$	$[Fe(\mathbf{2c})_2]^{2+}$	$[Fe(\mathbf{2d})_2]^{2+}$
BP86	+84.5	+88.7	+83.2	+85.0
B3LYP* [b]	–11.1	–3.3	–13.8	–16.9

[a] Structures optimized in ORCA on the BP86-D3/TZVP level of theory; [b] single-point calculations in the BP86-optimized positions on the B3LYP*-D3/TZVP level of theory.

4 NMR elucidation

4.1 Proton labelling



$[Fe(\mathbf{2a})_2]^{2+}$ $[Fe(\mathbf{2b})_2]^{2+}$ $[Fe(\mathbf{2c})_2]^{2+}$ $[Fe(\mathbf{2d})_2]^{2+}$

Scheme 1-SI: Labelling of protons for ^1H NMR discussion, labelling of nitrogen atoms and rings for x-ray structure discussion

4.2 General remarks and RT spectra of $[Fe(\mathbf{2b\text{-}d})_2]^{2+}$

All spectra were recorded on a Bruker Avance III 500 MHz spectrometer operated with the Topshim2.1 software package. Chemical shifts are referenced internally to the residual solvent protons relative to TMS (TMS = 0 ppm). Linewidths were measured by fitting to Lorenzian shaped curve in Topshim2.1 package. No corrections for possible H-H coupling were applied. The linewidths are generally susceptible to temperature variations and should be seen as good estimations with error in 10-30%. The longitudinal relaxation times T_1 were measured by the inversion recovery method. The sample temperatures were corrected by reference measurements with methanol and glycol samples using reported calibration functions.

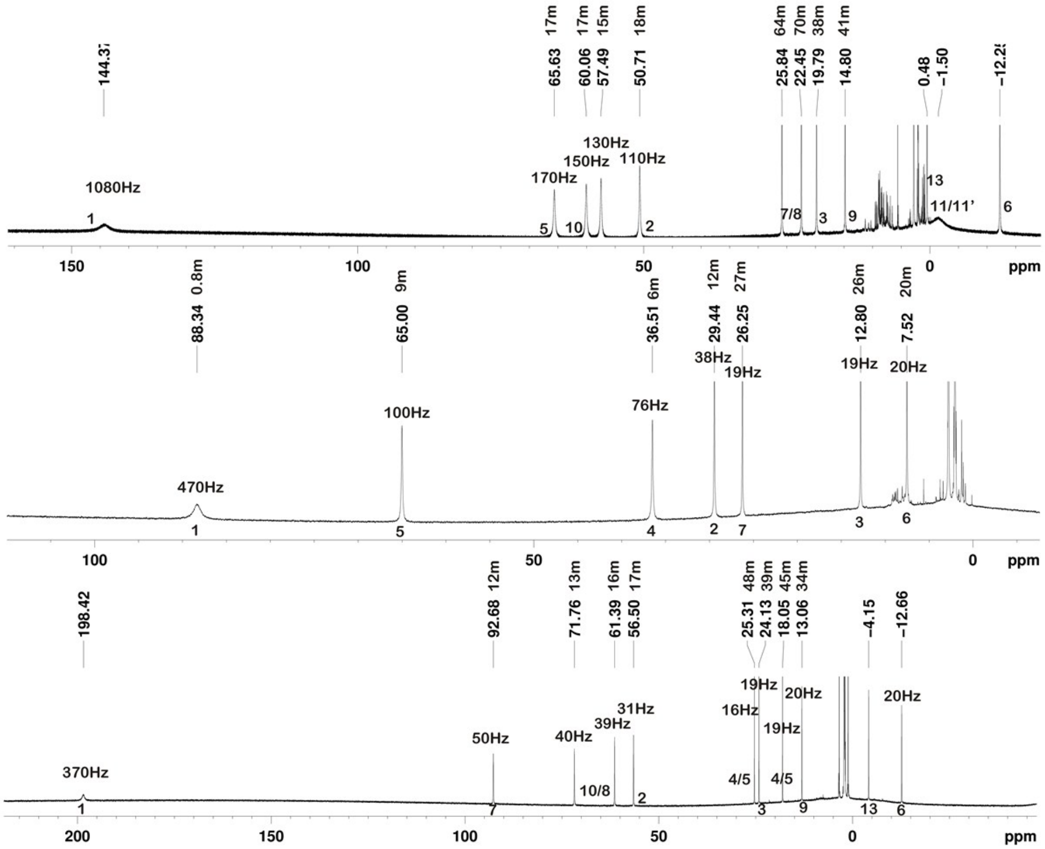


Figure 1-SI: RT ^{1}H NMR spectra of complexes (top) [Fe(**2b**)$_2$]$^{2+}$; (middle) [Fe(**2d**)$_2$]$^{2+}$ and (bottom) [Fe(**2c**)$_2$]$^{2+}$. The small numbers on horizontal lines without units represent the proton label, the numbers in vertical lines without units present the chemical shifts in ppm, T_1 times are given in units of ms (m) and the linewidths in units of Hz.

4.3 VT-^{1}H NMR study of [Fe(**2b**)$_2$]$^{2+}$

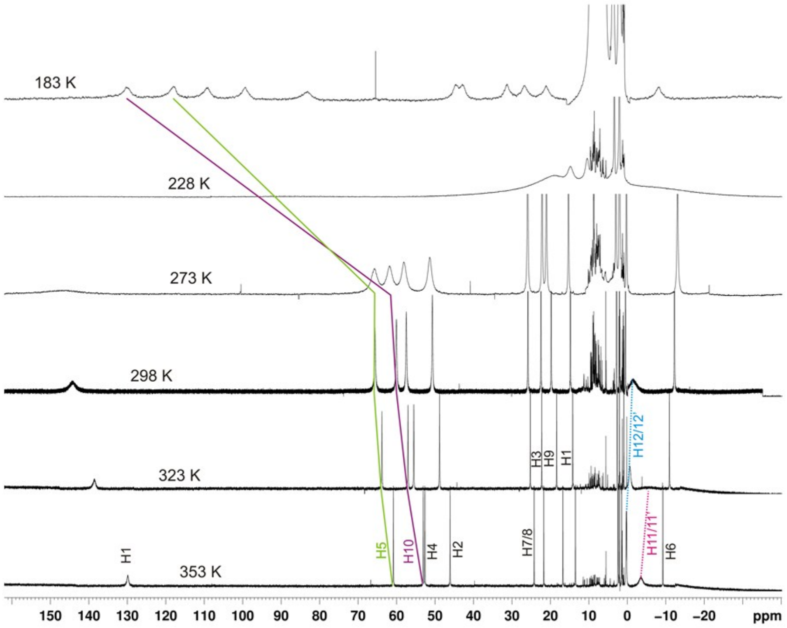


Figure 2-SI: VT NMR spectra of [Fe(**2b**)$_2$]$^{2+}$ in d_6-acetone solution. Spectra have been scaled to increase the visibility of broad and weak resonances.

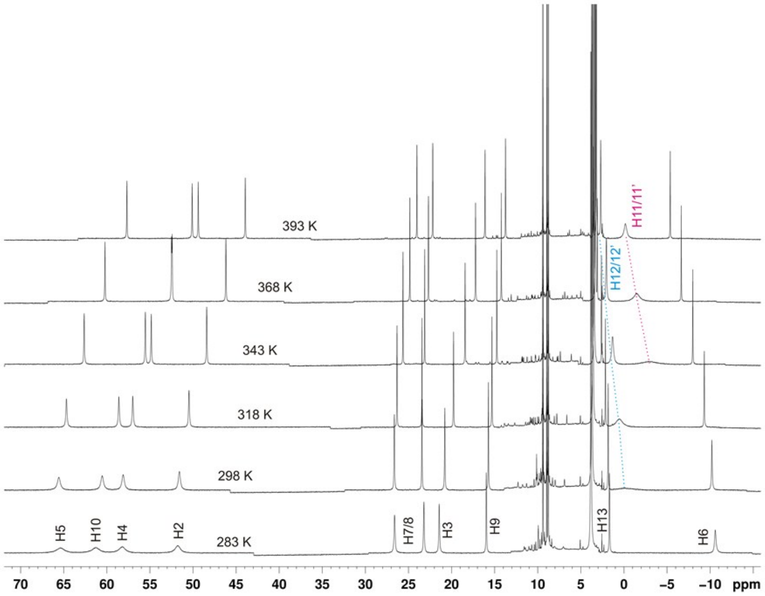


Figure 3-SI: VT ^{1}H NMR spectra of [Fe(**2b**)$_2$]$^{2+}$ in d_5-nitrobenzene.

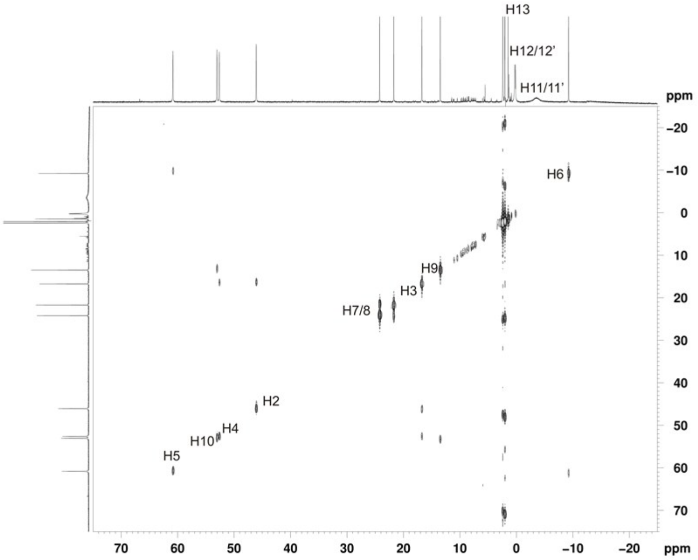


Figure 4-SI: ^{1}H,^{1}H COSY spectrum of [Fe(**2b**)$_2$]$^{2+}$ in acetone solution (thick wall tube 353 K)

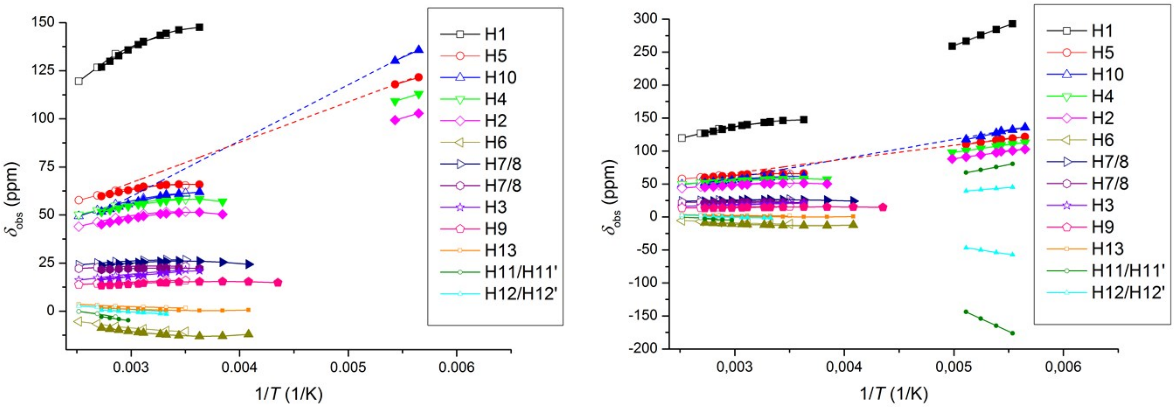


Figure 5-SI: Curie-plots of the chemical shift (left selected data, right all data) (empty symbols in d_5-nitrobenzene and filled symbols in d_6-acetone solution) vs. inverse temperature for [Fe(**2b**)$_2$]$^{2+}$. The chemical shift δ_{obs} does not follow a straight line which is the clear indication of a SCO, the estimated chemical shifts for protons H5 and H10 (d_6-acetone solution) are given as dashed lines. The lines end due to severe exchange broadening and overlap. The coalescence point for the HS and LS shift appears around T = 0.005 1/K (200K).

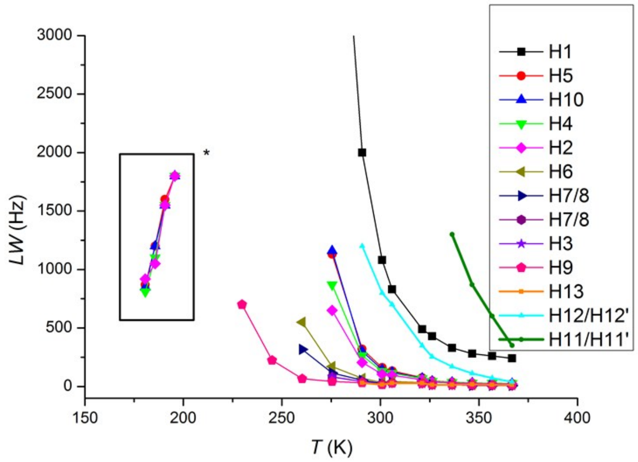


Figure 6-SI: Plot of the linewidths of proton resonance of complex [Fe(**2b**)$_2$]$^{2+}$ in d_6-acetone solution. Around the coalescence (200K) the large linewidths render the resonances unobservable. Similarly to [Fe(**2c**)$_2$]$^{2+}$ the rotation of the phenyl group is hindered this lead to increase of the line widths of *H*11 and *H*12 at substantial higher temperatures than for SCO associated exchange broadening. Due to the large linewidths a more elaborate interpretation is not advisable. With decreasing temperatures -below the coalescence- the linewidths drop and the HS signals become visible again (* boxed). In line with the discussion in the paper, those resonances have similar linewidths according to the dominance of k_{HSLS} (with slight contributions of $R_{2\mathrm{HS}}$). Due to the small signals intensity (HS fraction < 5%) we refrain from more quantitative interpretation.

4.4 VT-^{1}H NMR study of [Fe(**2c**)$_2$]$^{2+}$

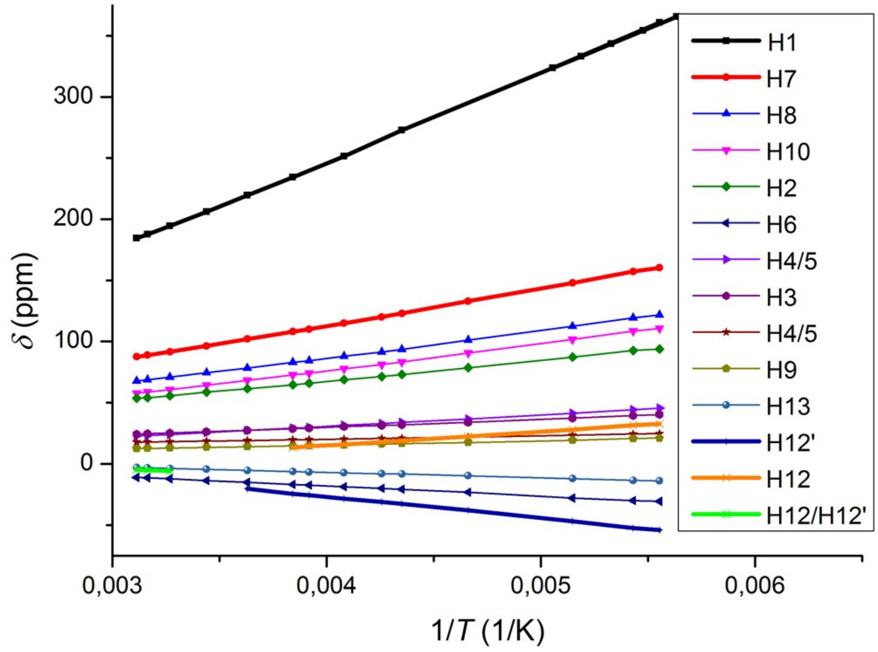


Figure 7-SI: Plot of the chemical shifts of complex [Fe(**2c**)$_2$]$^{2+}$ vs. 1/*T* in d_6-acetone, note that blow 280 K (0.0036 1/K) the slope of the lines for *H*12 and *H*12' stand out.

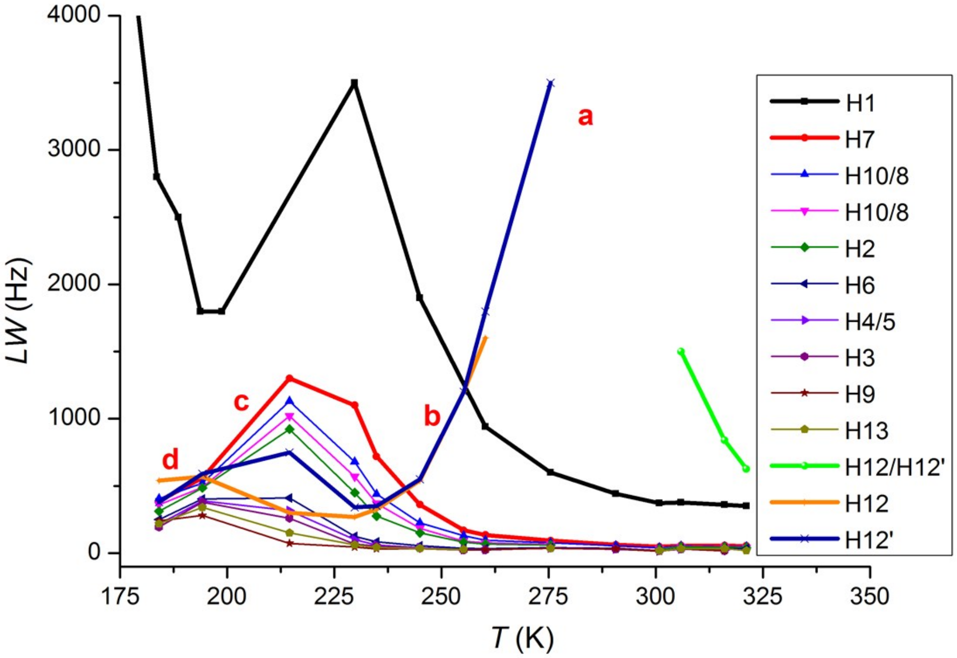


Figure 8-SI: Plot of the linewidths for $[Fe(\mathbf{2c})_2]^{2+}$ in d_6-acetone. The coalescence between proton *H*12 and *H*12' is found at point **a**, below the coalescence at point **b** the linewidths of these two protons are equivalent to $k_r = \pi \cdot LW$. Depending on $\Delta\omega$ the "SCO hump" appears around 210 K the low temperature shoulder (point c) again give the rate constant k_{HSLS} for the decay of the HS state to the LS state. Shortly above the freezing point of the solvent (point d) the Curie relaxation becomes dominant and the linewidths reflect the distance of the protons to the Fe^{2+} ion ~$1/r^6$.

4.5 VT-^{1}H NMR study of [Fe(**2d**)$_2$]$^{2+}$

Table 6-SI: Selected data from ^{1}H NMR (RT) and solid state structures of [Fe(**2a**)$_2$]$^{2+}$ and [Fe(**2d**)$_2$]$^{2+}$.

	[Fe(**2d**)$_2$]$^{2+}$						[Fe(**2a**)$_2$]$^{2+}$			
Proton	r (Fe-H) (Å)	averaged with	1/r^6 (1/Å^6) (Fe-H) average	δ (ppm) RT/d_6-acetone	T_1 (ms) RT/d_6-acetone	LW (Hz)	*Proton*	δ (ppm) RT/d_6-acetone	averaged (ppm)	over
*H*1	3.43	*H*1/*H*1’	$4.71\cdot10^{-4}$	88.23	0.83	466	*H*1	198	102.5	*H*1/*H*14
*H*2	5.41	*H*2/*H*2’	$3.48\cdot10^{-5}$	29.43	12	38	*H*2	63.55	35.275	*H*2/*H*13
*H*3	6.1	*H*3/*H*3’	$1.78\cdot10^{-5}$	12.79	26	19	*H*3	15.56	11.28	*H*3/*H*12
*H*4	5.197	*H*4/*H*4’	$4.77\cdot10^{-5}$	36.46	6	76	*H*4	63.55	35.275	*H*4/*H*11
*H*5	5.164	*H*5/*H*5’	$5.00\cdot10^{-5}$	64.96	9	97	*H*5	91.73	74.635	*H*5/*H*10
*H*6	5.873	*H*6/*H*6’	$2.35\cdot10^{-5}$	7.52	20	20	*H*6	−20.74	0.75	*H*6/*H*9
*H*7	6.306	*H*7/*H*7’	$1.58\cdot10^{-5}$	26.24	27	19	*H*7	26.09	21.21	*H*10/*H*11
*H*7’	6.326						*H*8	16.33		
*H*6’	5.943						*H*9	22.24		
*H*5’	5.26						*H*10	57.54		
*H*4’	5.311							7[a]		
*H*3’	6.283							7[a]		
*H*2’	5.683							7[a]		
*H*1’	3.808							7[a]		

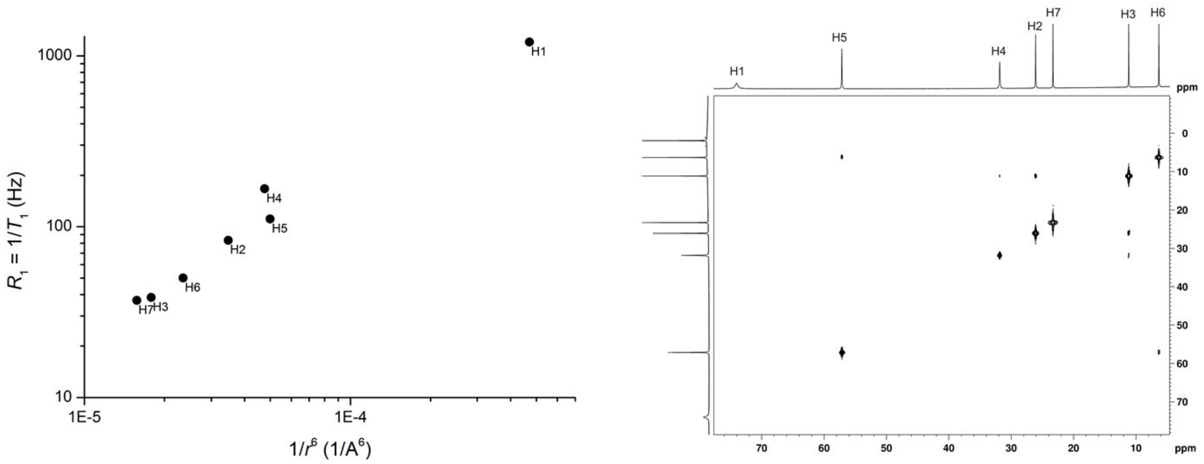


Figure 9-SI: left) plot of the distance Fe-H vs. the relaxivity at ambient temperature (d_6-acetone) for [Fe(**2d**)$_2$]$^{2+}$. Distance is given as 1/(Fe-H)^6 to account for dependence of R_1 on the square of the dipolar coupling (1/r^3); right) COSY spectrum of [Fe(**2d**)$_2$]$^{2+}$ in d_3-acetonitrile @348 K.

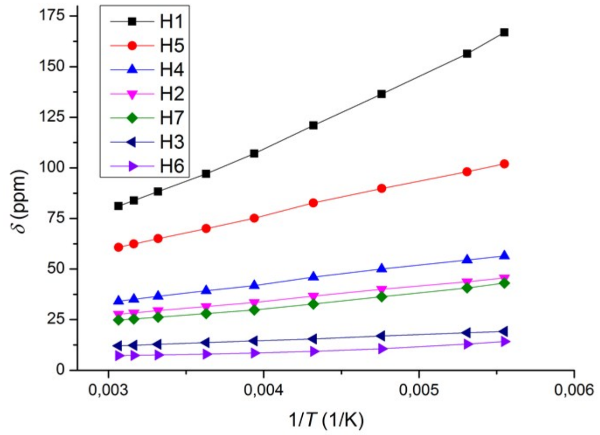


Figure 10-SI The plot of the chemical shift δ vs. 1/T shows the Curie dependence in [Fe(**2d**)$_2$]$^{+2}$ as straight lines.

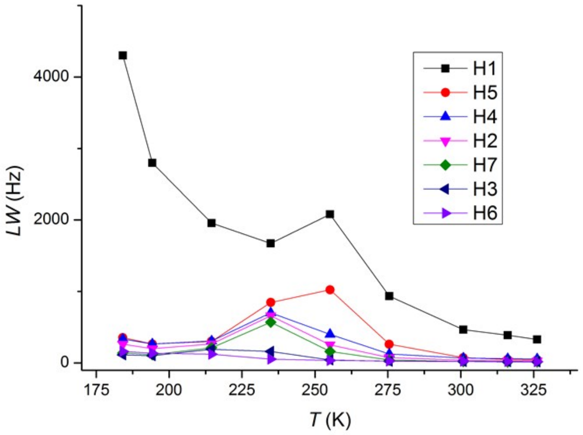


Figure 11-SI: Plot of the linewidths LW at half height vs. *T*. The humps are the manifestation of SCO in $[Fe(\mathbf{2d})_2]^{2+}$, the low temperature slopes account for $R_{2(HS)}+k_{HSLS}$.

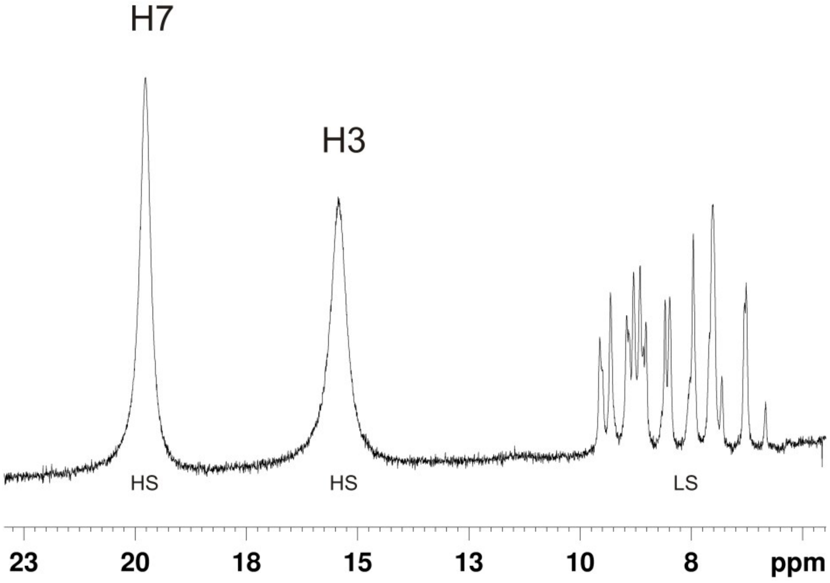


Figure 12-SI: The ^1H NMR spectrum of $[Fe(\mathbf{2d})_2](ClO_4)_2$ in d_6-acetone @ 178 K shows two sets of resonances one for the HS complex -represented by the two large and broad signals (@19 ppm and @15.5 ppm)- and the resonances around 8 ppm characteristic for aromatic protons of LS Fe^{2+} complexes.

Table 7-SI: longitudinal relaxivities R_1 for $[Fe(\mathbf{2d})_2]^{2+}$ in d_6-acetone

		T_1 (ms) @ (nominal)							
shift RT ppm	Proton	313 K	298 K	273 K	253 K	233 K	213 K	193 K	183 K
84.1	H1	0.94	0.8	0.64		0.36	0.24	0.164	0.145
29.0	H2	14	12.33	9.6	7.6	5.4	4	3	2.4
12.3	H3	29	26.2	21	17.1	13.3	10.4	7.9	6.7
36.0	H4	6.8	6.17	5.3	4.4	3.4	2.9	2.6	2
64.7	H5	10.4	9.2	7.2		4.2	3.1	2.3	1.75

6.2	H6	22.5	20	15.5	11.8	8.8	6.5	4.6	3.8
25.3	H7	31	27.6	21	16.2	12.3	8.4	5.8	4.4

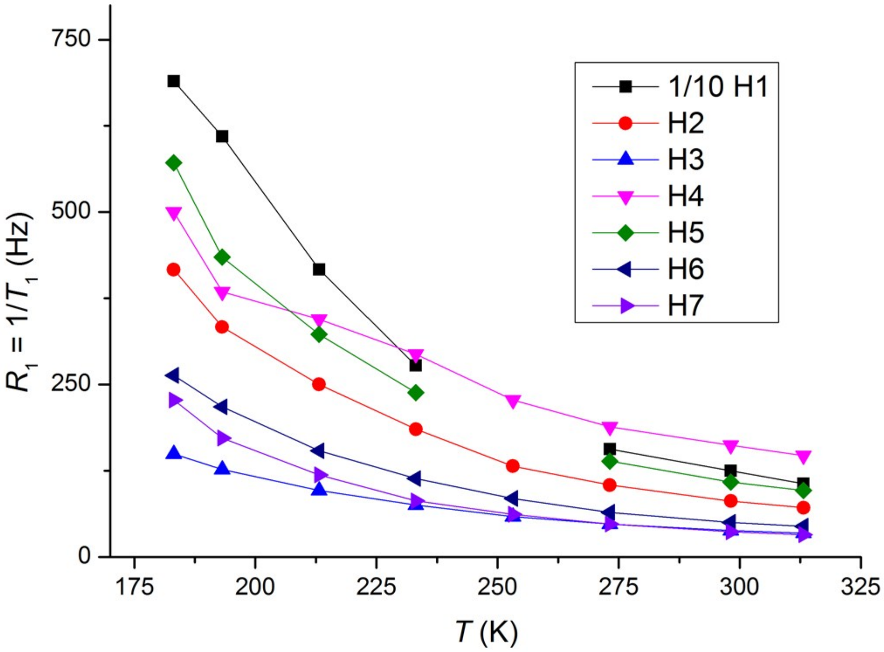


Figure 13-SI: Longitudinal relaxivity R_1 vs. T for [Fe(**2d**)$_2$]$^{2+}$ in d_6-acetone solution. The relaxivity of H1 was scaled by a factor of 10 for clarity.

4.6 Qualitative elucidation of the HS-LS relaxation

In order to obtain k_{HSLS} from the low-temperature slope of the SCO humps, the transversal relaxivities $R_{2(\mathrm{HS})}$ of the pure HS state must be calculated. For the elucidation the protons $H7$ (Fe-H 5.066 Å) [Fe(**2a**)$_2$]$^{2+}$, $H5$ (Fe-H 5.013 Å) [Fe(**2b**)$_2$]$^{2+}$, H7 (Fe-H 5.087 Å) [Fe(**2c**)$_2$]$^{2+}$ and H5 (Fe-H 5.164/5.260 Å) [Fe(**2d**)$_2$]$^{2+}$ were chosen. They are in similar distance to the paramagnetic Fe^{2+} and show large chemical shifts. Due to the similar electronic structure (T_1 times) and size of complexes [Fe(**2a**-**c**)$_2$]$^{2+}$ $R_{2(\mathrm{HS})}$ of H7-[Fe(**2a**)$_2$]$^{2+}$ was modelled according to previously published methods[7] using NMR$_2$SCO[19] and this value was transferred to $H5$-[Fe(**2b**)$_2$]$^{2+}$ and H7-[Fe(**2c**)$_2$]$^{2+}$. A transfer to H5-[Fe(**2d**)$_2$]$^{2+}$ was not justified due to the substantially larger dipolar contribution to $R_{2(\mathrm{HS})}$. Therefore $R_{2(\mathrm{HS})}$ for H5-[Fe(**2d**)$_2$]$^{2+}$was calculated separately based on the T_1 values using NMR$_2$SCO. The T(1ms) and T(0.5ms)-lines were calculated by the addition of 1000Hz and 2000Hz to $R_{2(\mathrm{HS})}$, respectively.

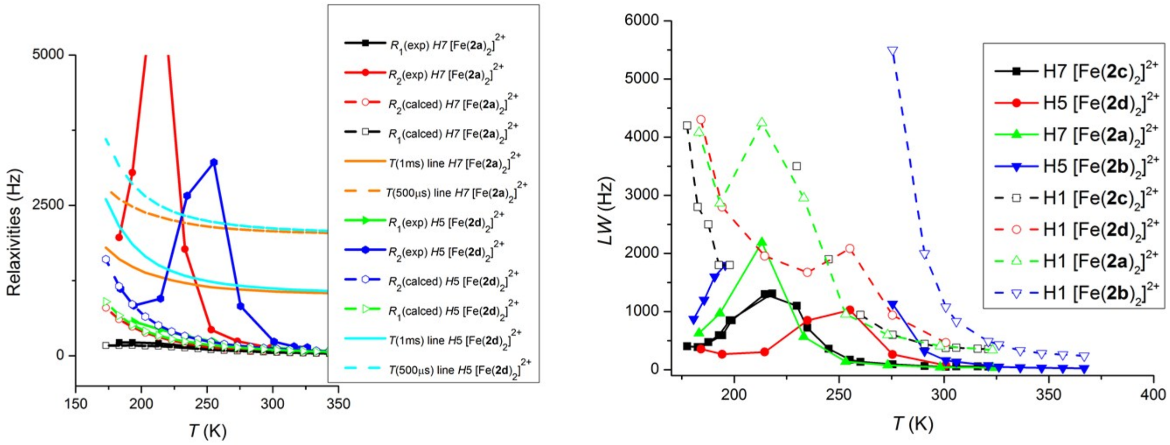
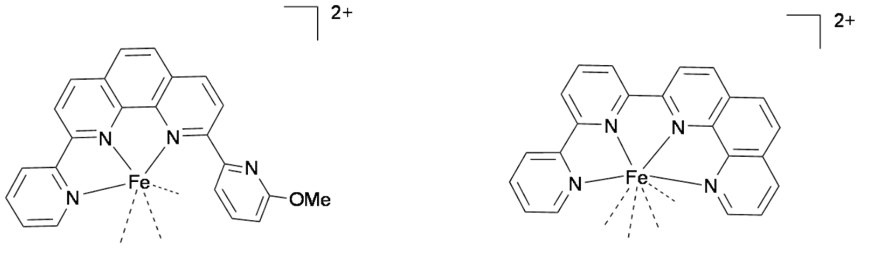


Figure 14-SI: left) Plot of experimental and modelled relaxivities for *H*7-$[Fe(\mathbf{2a})]^{2+}$ (black (R_1) and red lines) and *H*5-$[Fe(\mathbf{2d})]^{2+}$ (green (R_1) and blue lines) in d_6-acetone solution. SCO humps are clearly visible the crossings, the low-temperature slope reports on k_{HSLS}. In the *T*(1ms) and *T*(0.5ms) lines give the linewidths that correspond to $\tau_{HSLS} = 1/k_{HSLS}$ of 1ms and 0.5ms respectively (orange and light blue lines). Right) The plots of *LW* vs. *T* including *H*1 protons for all complexes shows clearly the SCO humps and the qualitative difference in k_{HSLS}.

4.7 ^{1}H NMR elucidation of related complexes $[Fe(\mathbf{2e,f})_2]^{2+}$



$[Fe(\mathbf{2e})_2]^{2+}$

$[Fe(\mathbf{2f})_2]^{2+}$

Scheme 2-SI: Suggested molecular structure of complexes $[Fe(\mathbf{2e,f})]^{2+}$; ^{1}H NMR spectra are shown and discussed below.

In the course of this project, compounds of two additional bis-meridionally coordinated complexes $[Fe(\mathbf{2e})_2]^{2+}$ and $[Fe(\mathbf{2f})_2]^{2+}$ were prepared. Synthesis of ligands **2e** and **2f** follows the general protocol starting from 2-brom-6-methoxypyridine and 6-bromo-2,2'-bipyridine. Both the ligands and the derived complexes were not completely characterized. However, by knowledge of the basic of ^{1}H NMR spectroscopy on Fe^{2+} SCO complexes -published in this and previous[7,20] contributions- an excellent forecast on the SCO properties and the coordination sphere is possible.

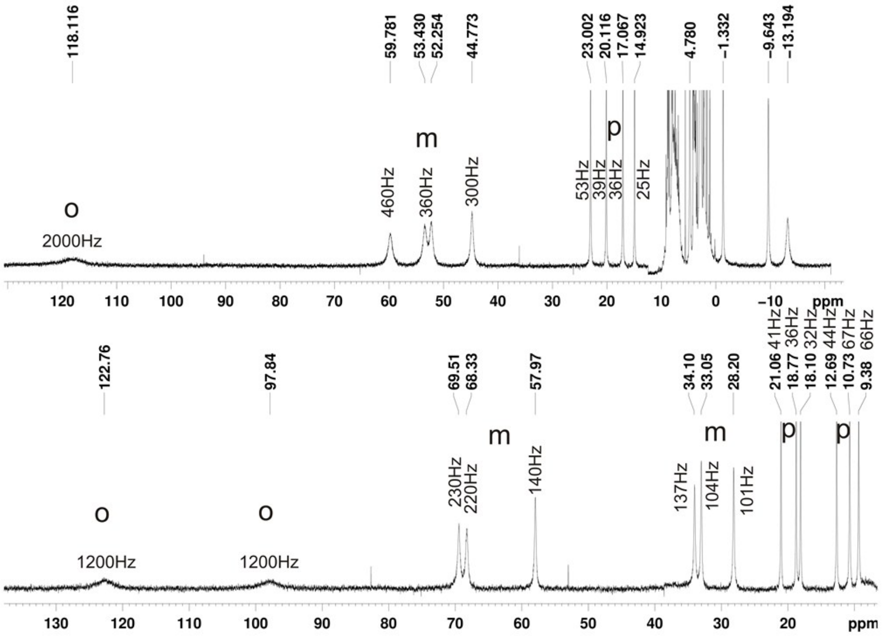


Figure 15-SI: (top) ^{1}H NMR spectrum of [Fe(**2e**)](BF_4)$_2$ in d_3-acetonitrile solution. The complex shows SCO properties akin to [Fe(**2b**)]$^{2+}$ this can be seen by the striking similarity to spectra of [Fe(**2b**)$_2$]$^{2+}$. The rather broad lines for *H*1 (120 ppm) and *meta* protons (around 50 ppm) are the result of the exchange broadening. Note that the linewidths depend on the paramagnetic shift (more precisely $\Delta\omega^2$) Bottom) ^{1}H NMR spectrum of complex [Fe(**2f**)$_2$]$^{2+}$ in d_3-acetonitrile solution. The forecast for this complex is a rather regular bis-meridionally N8 coordination with a trigonal dodecahedral geometry. In contrast to the resonances of [Fe(**2e**)$_2$]$^{2+}$ the linewidths depend on the distance r = Fe···H (exactly 1/r^6). This becomes evident for the *meta* protons three around 65 ppm and three around 30 ppm with similar distance to the Fe^{2+} and hence similar linewidths. Exchange broadening would results in 4 time larger linewidths for the *meta* protons around 65 ppm ($LW \sim \Delta\omega^2$).

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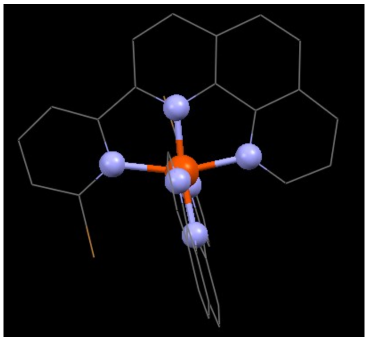
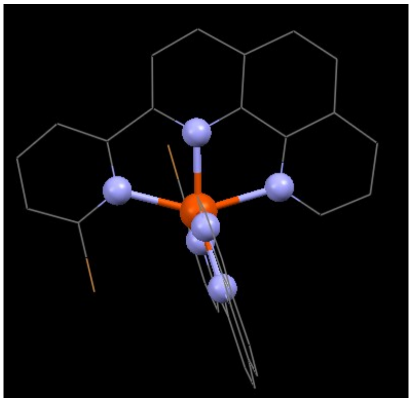
5.1 Cartesian coordinates of DFT optimized structures

Table 8-SI: Cartesian coordinates of the optimized structure of LS [Fe(**2a**)$_2$]$^{2+}$ (BP86-D3/TZVP).



C	6.836894	0.446975	4.519015
H	6.344988	0.504685	3.549400
C	6.291107	-0.329899	5.558087
H	5.366204	-0.874295	5.370860
C	6.912530	-0.394503	6.797821
H	6.486268	-0.990220	7.606052
C	8.110519	0.330954	6.997169
C	8.587663	1.076642	5.896074
C	8.871589	0.389579	8.218334
H	8.515189	-0.180308	9.077347
C	10.018458	1.141190	8.325961
H	10.564303	1.169312	9.269918
C	10.511725	1.903938	7.214367
C	9.780527	1.821765	6.011707
C	11.659929	2.739175	7.190493
H	12.276626	2.844399	8.083942
C	11.989020	3.434140	6.033172
H	12.861469	4.086179	6.023846
C	11.198557	3.293099	4.869460
C	11.388566	3.900193	3.558361
C	12.454927	4.741919	3.251772
H	13.183627	4.992295	4.021040
C	12.583283	5.245471	1.959293
H	13.409806	5.904392	1.692822
C	11.636304	4.884034	1.008112
H	11.692737	5.243575	-0.017276
C	10.583507	4.039892	1.383169
Br	9.342685	3.610874	0.009966
C	8.179037	4.823838	4.986629
H	9.084759	4.680859	5.572747
C	7.307492	5.896343	5.255398
H	7.560559	6.584349	6.061710
C	6.146120	6.069868	4.514744
H	5.466983	6.896721	4.727244
C	5.856678	5.152420	3.477329
C	6.793168	4.114039	3.273857
C	4.694095	5.172880	2.627887
H	3.962017	5.968559	2.773660
C	4.487600	4.224564	1.653193
H	3.589849	4.266458	1.035002
C	5.432350	3.165160	1.437524
C	6.583976	3.164643	2.251041
C	5.337778	2.111740	0.490112
H	4.476690	2.053461	-0.177105
C	6.335565	1.147132	0.423203
H	6.251518	0.331075	-0.293901
C	7.458510	1.223829	1.278699
C	8.617474	0.343372	1.344436
C	8.797615	-0.750590	0.501341
H	8.033683	-0.996832	-0.234557
C	9.960527	-1.511367	0.601255
H	10.126611	-2.370616	-0.048443
C	10.913677	-1.147743	1.545514
H	11.842503	-1.702607	1.660952
C	10.666813	-0.042640	2.369704
Br	12.028835	0.363175	3.630504
N	7.971513	1.146283	4.670503
N	10.129372	2.477628	4.879765
N	10.423679	3.540294	2.624766
N	7.938802	3.936601	4.009736
N	7.565725	2.237816	2.154343
N	9.551529	0.711891	2.305900
Fe	8.963160	2.334810	3.410240

Table 9-SI: Cartesian coordinates of the optimized structure of HS [Fe(**2a**)$_2$]$^{2+}$ (BP86-D3/TZVP).



C	7.171293	0.287466	4.567196
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H	6.758830	-0.875711	7.749034
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C	8.797621	1.182975	5.941669
C	8.983531	0.678434	8.341219
H	8.599273	0.150161	9.214887
C	10.085980	1.485116	8.456504
H	10.586965	1.598868	9.418693
C	10.606164	2.181577	7.317612
C	9.939194	2.036261	6.071563
C	11.743139	3.023752	7.328462
H	12.293768	3.175420	8.258139
C	12.163760	3.647958	6.162322
H	13.044524	4.288024	6.177451
C	11.442569	3.444136	4.965857
C	11.777921	4.028888	3.651985
C	12.872044	4.862533	3.423723
H	13.543158	5.133798	4.236729
C	13.103678	5.344698	2.131329
H	13.956392	5.993494	1.928787
C	12.236004	4.992705	1.101061
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C	11.159802	4.158593	1.422232
Br	9.927099	3.664828	0.052267
C	8.170614	5.047975	4.604784
H	9.115906	5.008236	5.146831
C	7.242441	6.075792	4.856072
H	7.477445	6.838228	5.598512
C	6.045506	6.106549	4.157493
H	5.312688	6.895126	4.336082
C	5.782505	5.098681	3.200142
C	6.780276	4.106396	3.018427
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C	4.391874	4.044070	1.477993
H	3.478674	4.019453	0.881699
C	5.384515	3.032161	1.268784
C	6.565025	3.067673	2.058102
C	5.286127	1.978664	0.329295
H	4.400051	1.900139	-0.303106
C	6.313678	1.054512	0.203447
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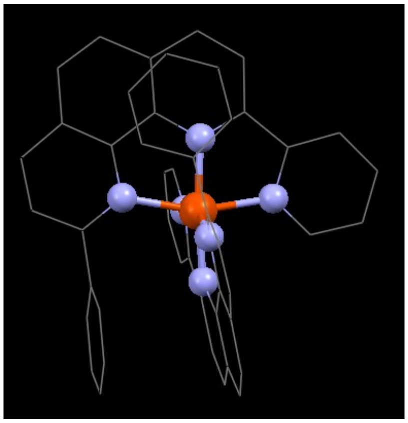
C	8.630029	0.274666	0.992308
C	8.758410	-0.813497	0.129526
H	7.961273	-1.067732	-0.567275
C	9.929930	-1.577133	0.164608
H	10.053432	-2.429180	-0.504467
C	10.940463	-1.243659	1.062469
H	11.867710	-1.810161	1.123346
C	10.721840	-0.142715	1.897654
Br	12.064797	0.340839	3.163593
N	8.238721	1.081618	4.702126
N	10.359031	2.655811	4.950529
N	10.926059	3.679313	2.641408
N	7.955672	4.078398	3.709057
N	7.549315	2.156383	1.925951
N	9.620141	0.604221	1.875481
Fe	9.243248	2.348136	3.180245

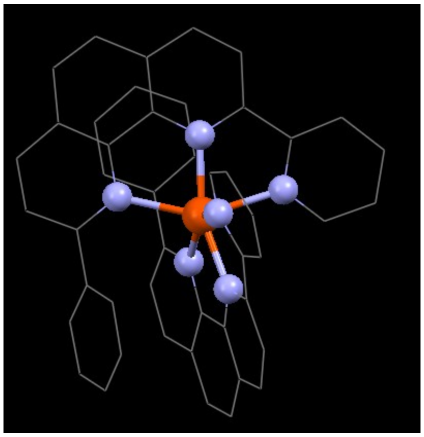
Table 10-SI: Cartesian coordinates of the optimized structure of LS [Fe(**2b**)$_2$]$^{2+}$ (BP86-D3/TZVP).



Fe	0.699201	14.756018	3.007343
C	-1.546501	13.894625	4.961852
C	-2.414737	12.895556	5.470897
H	-3.081645	13.174993	6.286222
C	-2.415451	11.607036	4.965294
H	-3.077380	10.844717	5.379010
C	-1.550597	11.301377	3.890456
C	-0.728029	12.351747	3.427513
C	-1.454929	10.027680	3.228784
H	-2.079127	9.210274	3.592596
N	-0.686544	13.622003	3.960943
C	-0.961979	16.890593	7.202930
H	-0.341029	17.168874	8.055093
C	-1.921364	17.782376	6.713862
H	-2.047675	18.758452	7.183382
C	-2.734967	17.413665	5.639517
H	-3.494974	18.101236	5.266877
C	-2.588718	16.155265	5.051598
H	-3.233927	15.858382	4.222766
C	-1.621520	15.261986	5.535821
C	-0.812789	15.630597	6.619076
C	1.681803	13.148578	0.900246
C	1.858134	11.929711	0.210549
H	2.573967	11.868516	-0.608658
C	1.123889	10.809623	0.576841
H	1.255668	9.869604	0.040277
C	0.209248	10.883268	1.659794
C	0.097944	12.135941	2.300493
C	-0.610335	9.821243	2.164074
H	-0.557558	8.840625	1.689438
N	0.796180	13.228145	1.915361
C	2.560535	16.594767	1.553654
H	2.258429	17.322175	2.303383
C	3.471703	16.936822	0.557619
H	3.884804	17.944492	0.534352
C	3.839284	15.979072	-0.390850
H	4.551755	16.219459	-1.180077
C	3.272891	14.708425	-0.311945
H	3.531285	13.937969	-1.037869
C	2.361310	14.421754	0.707113
N	2.005661	15.368202	1.644757
C	1.924345	16.349782	4.994257
C	2.191218	17.566628	5.658019
H	2.992241	17.617853	6.395182
C	1.438916	18.697354	5.369470
H	1.641133	19.635665	5.886640
C	0.412786	18.636111	4.390930
C	0.215060	17.384427	3.769313
C	-0.439520	19.710123	3.973975
H	-0.320661	20.690617	4.436761
N	0.934012	16.282331	4.080608
C	2.685002	12.894967	4.249126
H	2.294989	12.173125	3.535385
C	3.697324	12.541169	5.137080
H	4.100791	11.529618	5.112051
C	4.178338	13.492831	6.039522
H	4.972894	13.243927	6.743016
C	3.619675	14.769415	6.025913
H	3.966355	15.536125	6.718290
C	2.603780	15.067981	5.114684
N	2.136654	14.127272	4.221660
C	-1.735085	15.647402	1.307612
C	-2.641510	16.657687	0.896562
H	-3.399047	16.386502	0.161528
C	-2.567326	17.946930	1.394536
H	-3.260286	18.718028	1.054423
C	-1.583507	18.241815	2.365002
C	-0.731146	17.179664	2.739194
C	-1.397235	19.515117	3.007533
H	-2.045024	20.341200	2.710493

N	-0.766065	15.908504	2.207180
C	-3.031798	12.146305	0.737670
H	-3.759995	11.465832	1.180151
C	-2.333783	11.773926	-0.413806
H	-2.518850	10.802116	-0.872540
C	-1.416183	12.656515	-0.991622
H	-0.886871	12.375762	-1.902622
C	-1.194152	13.910991	-0.419483
H	-0.496765	14.612229	-0.882034
C	-1.886117	14.283366	0.740813
C	-2.812023	13.399216	1.314071
H	-3.368756	13.698689	2.203969
H	-0.081044	14.922960	7.012960

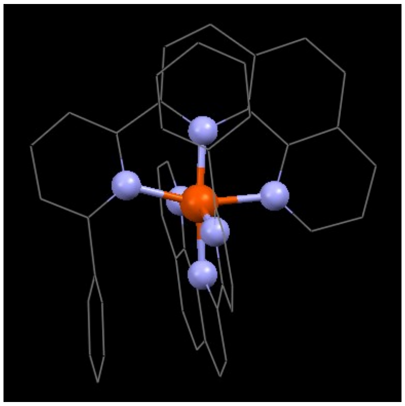
Table 11-SI: Cartesian coordinates of the optimized structure of HS [Fe(**2b**)$_2$]$^{2+}$ (BP86-D3/TZVP).



Fe	0.039289	14.744622	2.536567
C	-1.428248	13.728371	5.217402
C	-1.611993	12.802895	6.275517
H	-2.198377	13.107519	7.141927
C	-1.108820	11.519925	6.175095
H	-1.280546	10.792726	6.970834
C	-0.374937	11.145415	5.024213
C	-0.181459	12.147442	4.041766
C	0.196297	9.846688	4.816074
H	0.021033	9.075072	5.567565
N	-0.708014	13.401986	4.130233
C	-3.469521	16.730257	4.201436
H	-4.110391	17.038414	3.374322
C	-3.279875	17.580343	5.295388
H	-3.762582	18.557698	5.317512
C	-2.491532	17.167092	6.375522
H	-2.351274	17.826133	7.232871
C	-1.897382	15.904985	6.365877
H	-1.287382	15.580621	7.210453
C	-2.056936	15.061992	5.253135
C	-2.849556	15.481113	4.170540
C	1.734649	12.751441	1.039726
C	2.317184	11.491830	0.764242
H	2.984380	11.369147	-0.088028
C	2.055862	10.416840	1.596321
H	2.511500	9.445683	1.398502
C	1.222442	10.583491	2.731771
C	0.650688	11.867001	2.912776
C	0.956169	9.570557	3.707616
H	1.386095	8.577866	3.567802
N	0.900200	12.902704	2.080049
C	1.760196	16.318467	0.353927
H	1.311433	17.180116	0.848721
C	2.572060	16.473789	-0.767903
H	2.775175	17.469506	-1.160314
C	3.107274	15.332494	-1.370997
H	3.733971	15.414963	-2.259258
C	2.830943	14.083239	-0.818146
H	3.240283	13.181247	-1.270961
C	2.023686	14.002196	0.323298
N	1.482471	15.117620	0.892253
C	1.610067	15.696387	5.189875
C	1.831951	16.596013	6.263411
H	2.446706	16.269526	7.101816
C	1.329715	17.882016	6.210419
H	1.530475	18.589911	7.016625
C	0.559228	18.285486	5.093684
C	0.328948	17.307251	4.095288
C	-0.012256	19.591093	4.934663
H	0.191708	20.344118	5.697601
N	0.853755	16.049458	4.136192
C	3.623881	12.728000	4.033417
H	4.238554	12.443339	3.178528
C	3.474105	11.850573	5.111983

H	3.961896	10.875517	5.094892
C	2.719569	12.233233	6.226740
H	2.610256	11.552855	7.071927
C	2.120453	13.492452	6.267657
H	1.537754	13.793408	7.139670
C	2.239969	14.362986	5.171575
C	2.998020	13.974206	4.053563
C	-1.685090	16.783201	1.141633
C	-2.269121	18.051739	0.914062
H	-2.960952	18.198494	0.085584
C	-1.976771	19.104951	1.763669
H	-2.432913	20.082742	1.603123
C	-1.109396	18.907822	2.868497
C	-0.539226	17.617558	3.001238
C	-0.806620	19.896582	3.858476
H	-1.235377	20.894260	3.755661
N	-0.820622	16.603815	2.152359
C	-1.744354	13.234158	0.366826
H	-1.284310	12.358948	0.826397
C	-2.587910	13.110116	-0.735252
H	-2.805313	12.125500	-1.147468
C	-3.135710	14.268111	-1.293550
H	-3.787403	14.210236	-2.165691
C	-2.839615	15.502071	-0.716960
H	-3.258483	16.416387	-1.134925
C	-2.000339	15.551557	0.402813
N	-1.447634	14.420151	0.927662
H	-3.003562	14.806218	3.327811
H	3.120623	14.669467	3.222354

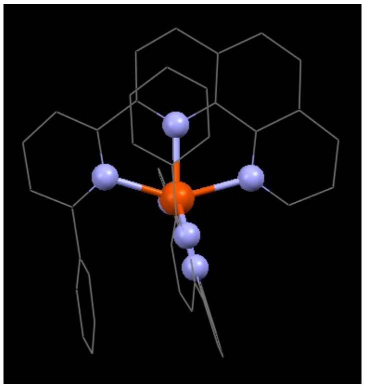
Table 12-SI: Cartesian coordinates of the optimized structure of LS [Fe(**2c**)$_2$]$^{2+}$ (BP86-D3/TZVP).



Fe	0.844211	14.859702	2.991208
C	-0.990389	15.066685	5.431312
C	-2.063677	14.605679	6.215399
H	-2.342054	15.172701	7.103129
C	-2.760129	13.458671	5.860554
H	-3.599965	13.106822	6.461315
C	-2.361476	12.751194	4.702803
C	-1.264756	13.279829	3.985970
C	-2.977806	11.557331	4.184580
H	-3.827701	11.137980	4.724649
N	-0.584005	14.423346	4.326703
C	4.934740	17.874174	3.494498
H	5.767135	17.885073	4.199570
C	4.238099	19.052143	3.212788
H	4.526449	19.985661	3.696926
C	3.188659	19.039420	2.287673
H	2.659408	19.962101	2.047594
C	2.831147	17.850773	1.650816
H	2.029916	17.842701	0.909631
C	3.521394	16.663905	1.939740
C	4.583903	16.683444	2.853322
C	0.812005	12.722956	1.128733
C	0.245458	11.575707	0.528398
H	0.670064	11.183007	-0.393791
C	-0.850360	10.950367	1.108963
H	-1.280735	10.062046	0.646059
C	-1.411004	11.470625	2.304508
C	-0.788758	12.620491	2.832573
C	-2.531010	10.948220	3.035105
H	-3.031343	10.052865	2.664132
N	0.296784	13.206760	2.274504
C	3.234220	15.428339	1.168391
H	-1.073713	14.372599	0.472319
C	4.104424	15.100301	0.116875
H	4.957196	15.752775	-0.066937
C	3.860125	13.988306	-0.684499
H	4.522257	13.741301	-1.514596
C	2.750013	13.200783	-0.397424

H	2.529206	12.309641	-0.983322
C	1.932358	13.538218	0.679898
N	2.153158	14.659070	1.459197
C	1.826962	16.809005	4.798916
C	1.791312	18.065694	5.445708
H	2.437488	18.251145	6.302218
C	0.934463	19.061483	4.996145
H	0.914345	20.031083	5.494597
C	0.082435	18.814300	3.888404
C	0.175375	17.533300	3.307386
C	-0.849384	19.728560	3.291715
H	-0.940510	20.733789	3.705238
N	1.034634	16.578037	3.736527
C	3.088518	13.419219	4.493134
H	-0.452706	15.973877	5.702550
C	4.156938	13.387551	5.403264
H	4.737954	12.469267	5.482330
C	4.438964	14.491008	6.203841
H	5.255477	14.463108	6.925946
C	3.653695	15.629915	6.057089
H	3.848625	16.525172	6.645838
C	2.628740	15.635365	5.112449
N	2.324886	14.531495	4.336612
C	-1.211171	15.403584	0.793747
C	-2.123308	16.248460	0.134050
H	-2.686392	15.850186	-0.709486
C	-2.309165	17.558263	0.554536
H	-3.024350	18.210274	0.051024
C	-1.550040	18.036084	1.648042
C	-0.648472	17.122354	2.238297
C	-1.622069	19.356622	2.216732
H	-2.317334	20.072199	1.775093
N	-0.476390	15.820527	1.835244
C	1.589283	10.096766	3.491068
H	0.799921	9.422404	3.825517
C	2.428918	9.724873	2.435582
H	2.292450	8.761058	1.944011
C	3.460291	10.576166	2.030768
H	4.129177	10.280889	1.221081
C	3.653878	11.798445	2.679386
H	4.471264	12.456618	2.378934
C	2.802672	12.181717	3.724905
C	1.773961	11.320389	4.135105
H	1.136567	11.601746	4.975073
H	5.139931	15.766113	3.056103

Table 13-SI: Cartesian coordinates of the optimized structure of HS [Fe(**2c**)$_2$]$^{2+}$ (BP86-D3/TZVP).

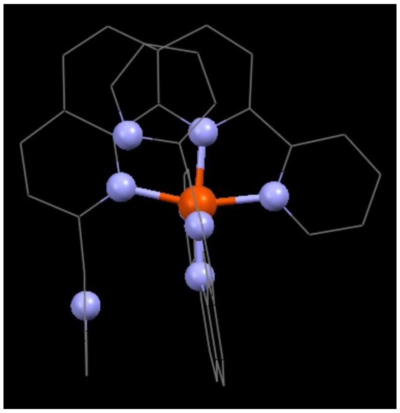


Fe	0.981790	14.833276	2.982622
C	-1.181173	14.744865	5.410808
C	-2.341011	14.290160	6.064090
H	-2.651019	14.764438	6.994568
C	-3.071401	13.244313	5.519670
H	-3.972924	12.875829	6.011090
C	-2.629437	12.649424	4.315276
C	-1.451367	13.180778	3.729137
C	-3.285068	11.544107	3.670835
H	-4.194565	11.145994	4.122426
N	-0.736631	14.210766	4.267904
C	5.005259	17.854132	3.126563
H	5.894445	18.049607	3.726747
C	4.047528	18.858464	2.944680
H	4.196332	19.840065	3.395678
C	2.917668	18.613830	2.158066
H	2.187311	19.405855	1.987185
C	2.730040	17.359665	1.577507
H	1.859133	17.165310	0.950708
C	3.688345	16.347573	1.758229
C	4.836209	16.606933	2.523750
C	0.790669	12.600860	0.957297
C	0.213462	11.500340	0.288595
H	0.688104	11.083643	-0.597920
C	-0.972692	10.957681	0.760943
H	-1.430127	10.110694	0.247483
C	-1.587125	11.488684	1.920340
C	-0.943721	12.601785	2.523155
C	-2.786945	10.985208	2.522079
H	-3.294369	10.139196	2.056837
N	0.195617	13.132958	2.033718
C	3.498369	15.044534	1.086865
H	-1.089836	14.762568	0.373685
C	4.477306	14.520149	0.226259
H	5.412713	15.061975	0.089891
C	4.210692	13.351196	-0.479387
H	4.948037	12.942364	-1.171069
C	2.980414	12.714417	-0.303137
H	2.753037	11.794715	-0.839088
C	2.066566	13.253577	0.601860
N	2.326564	14.401262	1.284957
C	1.838985	16.949465	4.957393
C	1.779141	18.172605	5.659288
H	2.476047	18.377606	6.470410
C	0.816134	19.111303	5.317994
H	0.757725	20.056900	5.859099
C	-0.084547	18.854402	4.256619
C	0.041692	17.596470	3.611340
C	-1.091138	19.762446	3.791539
H	-1.203362	20.725368	4.291549
N	0.966599	16.684251	3.975620
C	3.465325	13.706489	4.560971
H	-0.591754	15.563847	5.825525
C	4.659318	13.827891	5.291697
H	5.349356	12.985173	5.329541
C	4.910866	14.999068	5.999685
H	5.820355	15.102175	6.592593
C	3.977319	16.036666	5.954407
H	4.156060	16.964285	6.495375
C	2.832847	15.879039	5.173392
N	2.585511	14.729326	4.488384
C	-1.295900	15.729098	0.835936
C	-2.290359	16.577646	0.316581
H	-2.860446	16.261624	-0.556655
C	-2.528791	17.804744	0.917065
H	-3.293902	18.478937	0.528682
C	-1.758853	18.182117	2.041302

C	-0.784503	17.255677	2.494966
C	-1.893772	19.437004	2.728852
H	-2.650995	20.140894	2.379717
N	-0.553891	16.049705	1.900914
C	1.547814	10.593455	3.633733
H	0.612928	10.102124	3.905958
C	2.417807	9.990084	2.720444
H	2.159360	9.030043	2.272826
C	3.637234	10.600893	2.406226
H	4.323786	10.122762	1.706417
C	3.988031	11.812354	3.002668
H	4.941107	12.286298	2.761450
C	3.103397	12.437129	3.895690
C	1.881407	11.818576	4.210352
H	1.215609	12.287294	4.935934
H	5.585534	15.825395	2.661615

Table 14-SI: Cartesian coordinates of the optimized structure of LS [Fe(**2d**)$_2$]$^{2+}$ (BP86-D3/TZVP).

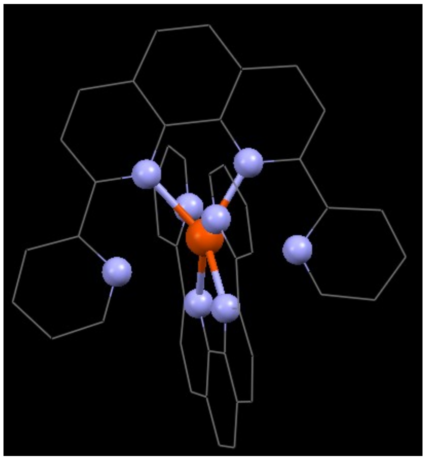
Fe	0.720324	14.755388	3.004579
C	-1.483434	13.853631	4.968005
C	-2.292494	12.832487	5.522176
H	-2.944388	13.095899	6.354727
C	-2.260879	11.539736	5.029903
H	-2.879644	10.757699	5.472176
C	-1.428061	11.258533	3.923017
C	-0.650580	12.329751	3.433776
C	-1.325462	9.991028	3.249284
H	-1.911910	9.154859	3.632841
N	-0.635789	13.602338	3.958386
C	-1.059585	16.833704	7.029737
H	-0.410800	17.110185	7.864381
C	-2.050583	17.709839	6.576581
H	-2.189717	18.677193	7.059285
C	-2.860027	17.311507	5.512553
H	-3.647936	17.964425	5.135248
C	-2.654533	16.049945	4.949722
H	-3.268319	15.682634	4.125471
C	-1.639790	15.245649	5.482861
N	-0.843665	15.617004	6.500688
C	1.661380	13.198699	0.839497
C	1.818149	11.996595	0.115718
H	2.502402	11.958717	-0.731419
C	1.114918	10.859158	0.491759
H	1.239451	9.930568	-0.066281
C	0.250191	10.897749	1.617160
C	0.141482	12.139582	2.278746
C	-0.524038	9.813212	2.145737
H	-0.468637	8.837251	1.661760
N	0.809159	13.249143	1.885130
C	2.610610	16.603573	1.604621
H	2.343322	17.302173	2.393991
C	3.509812	16.968189	0.605708
H	3.948487	17.965160	0.619133
C	3.833431	16.045581	-0.392481
H	4.535247	16.304056	-1.185519
C	3.240877	14.784961	-0.355583
H	3.469905	14.040282	-1.117451
C	2.344601	14.473973	0.670073
N	2.027728	15.387617	1.653517
C	1.870836	16.306572	5.067574
C	2.117405	17.512613	5.758735
H	2.882585	17.545623	6.533873
C	1.394224	18.656579	5.447064
H	1.585762	19.587160	5.982162
C	0.411744	18.618029	4.423091
C	0.227436	17.374570	3.782077
C	-0.409557	19.705072	3.977048
H	-0.300448	20.680702	4.452533
N	0.927118	16.263584	4.106020



C	2.705895	12.890464	4.234375
H	2.366232	12.195541	3.469855
C	3.676739	12.512877	5.158343
H	4.098057	11.509489	5.111242
C	4.091293	13.430053	6.126773
H	4.847985	13.160335	6.863561
C	3.516739	14.699390	6.135434
H	3.811700	15.438941	6.879175
C	2.547105	15.022597	5.184356
N	2.139239	14.114063	4.232449
C	-1.650348	15.678042	1.243942
C	-2.494969	16.707816	0.764311
H	-3.222245	16.453382	-0.006558
C	-2.420091	17.995529	1.267952
H	-3.073733	18.782367	0.888661
C	-1.494798	18.265394	2.301773
C	-0.682079	17.187222	2.716258
C	-1.321982	19.531233	2.963409
H	-1.940779	20.369801	2.640832
N	-0.721524	15.915617	2.186843
C	-3.004046	12.317504	1.061338
H	-3.675641	11.737705	1.698627
C	-2.536717	11.794369	-0.146879
H	-2.844112	10.799722	-0.468684
C	-1.687933	12.577494	-0.930892
H	-1.310390	12.207998	-1.884534
C	-1.350493	13.857138	-0.483857
H	-0.711617	14.513778	-1.076711
C	-1.866975	14.287936	0.742167
N	-2.678584	13.540805	1.514486

Table 15-SI: Cartesian coordinates of the optimized structure of HS [Fe(**2d**)$_2$]$^{2+}$ (BP86-D3/TZVP).

Fe	0.000048	14.745753	3.030068
C	-1.723548	13.005196	5.070874
C	-2.204061	11.819632	5.683422
H	-2.912783	11.878285	6.507211
C	-1.791992	10.586812	5.226050
H	-2.163098	9.670595	5.687174
C	-0.896275	10.513527	4.132307
C	-0.448847	11.747949	3.591111
C	-0.427989	9.286208	3.565094
H	-0.775415	8.345480	3.994255
N	-0.857005	12.956232	4.048609
C	-2.220273	16.594966	4.948694
H	-1.904439	17.392314	4.279368
C	-3.064534	16.887836	6.019924
H	-3.403854	17.910503	6.181889
C	-3.452618	15.848364	6.865457
H	-4.098217	16.033649	7.724317
C	-3.004503	14.561264	6.582322
H	-3.300350	13.733378	7.223795
C	-2.172325	14.347477	5.471456
N	-1.760945	15.363989	4.672683
C	1.723547	13.005204	0.989183
C	2.203856	11.819650	0.376458
H	2.912550	11.878304	-0.447355
C	1.791528	10.586833	0.833605
H	2.162442	9.670621	0.372313
C	0.895739	10.513538	1.927288
C	0.448541	11.747957	2.468684
C	0.427170	9.286214	2.494257
H	0.774410	8.345490	2.064936
N	0.857014	12.956236	2.011456
C	2.220412	16.594956	1.111476
H	1.904604	17.392297	1.780825
C	3.064675	16.887828	0.040249
H	3.404024	17.910489	-0.121694
C	3.452718	15.848366	-0.805318
H	4.098304	16.033656	-1.664186



C	3.004564	14.561272	-0.522215
H	3.300357	13.733398	-1.163727
C	2.172406	14.347478	0.588666
N	1.761050	15.363985	1.387459
C	1.723555	16.486383	5.070892
C	2.203912	17.671964	5.683526
H	2.912607	17.613343	6.507341
C	1.791679	18.904765	5.226249
H	2.162648	19.820996	5.687457
C	0.895945	18.978015	4.132518
C	0.448680	17.743573	3.591231
C	0.427494	20.205317	3.565399
H	0.774790	21.146059	3.994635
N	0.857026	16.535307	4.048613
C	2.220537	12.896649	4.948698
H	1.904775	12.099280	4.279378
C	3.064855	12.603846	6.019901
H	3.404270	11.581208	6.181851
C	3.452880	13.643347	6.865424
H	4.098526	13.458116	7.724260
C	3.004657	14.930410	6.582299
H	3.300466	15.758322	7.223756
C	2.172434	15.144132	5.471454
N	1.761090	14.127586	4.672702
C	-1.723507	16.486222	0.989177
C	-2.203923	17.671757	0.376495
H	-2.912612	17.613070	-0.447319
C	-1.791752	18.904595	0.833730
H	-2.162769	19.820791	0.372490
C	-0.896021	18.977932	1.927460
C	-0.448694	17.743533	2.468793
C	-0.427634	20.205277	2.494536
H	-0.774980	21.145987	2.065269
N	-0.856984	16.535235	2.011455
C	-2.220151	12.896439	1.111536
H	-1.904265	12.099132	1.780902
C	-3.064376	12.603480	0.040305
H	-3.403639	11.580789	-0.121627
C	-3.452485	13.642898	-0.805284
H	-4.098045	13.457542	-1.664158
C	-3.004426	14.930035	-0.522208
H	-3.300271	15.757871	-1.163745
C	-2.172288	15.143914	0.588672
N	-1.760894	14.127450	1.387498