

Electronic Supplementary Information (ESI)

Mimicking reactive high-valent diiron- μ_2 -oxo intermediates of nonheme enzymes by an iron tetracarbene complex

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1. General Considerations

Experimental Remarks. Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques. Dry, degassed acetonitrile was obtained from an Mbraun solvent purification system. Acetonitrile- d_3 was dried over phosphorous pentoxide, distilled, and stored over molecular sieves prior to use. All solvents were degassed by using at least three freeze/pump/thaw cycles. The diiron(III)-oxo complex **2** and thianthrenyl hexafluorophosphate were synthesized according to known literature procedures.^{1,2} All other reagents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker Advance DPX 400 (^1H NMR, 400.13 MHz; ^{13}C NMR, 100.53 MHz). Chemical shifts are reported in ppm and referenced to the residual signal of the deuterated solvent (acetonitrile- d_3 ; 1.94 ppm). Investigations concerning the magnetic susceptibility in solution were performed via Evans Method.^{3,4}

UV/Vis-spectra were recorded from liquid samples using a JASCO V-500 spectrometer. Elemental analyses (C/H/N) were obtained by the microanalytical laboratory at the Technische Universität München. Electrospray (ESI) mass spectrometry (MS) data were carried out on an LCQ-Fleet by Thermo Scientific. CV measurements were performed at $-40\text{ }^\circ\text{C}$ on a GRAMY reference 600 potentiostat and a DAQ electrochemical reaction vessel (3 mL) was used as electrochemical cell. Platinum electrodes were used as working/ counter electrodes, Ag/AgCl (3.4 M in KCl) was used as reference electrode (all from eDAQ) and ferrocene was used as internal standard. The potential was scanned with scan rates of 50 mV/s to 400 mV/s.

2. Single crystal X-ray diffraction:

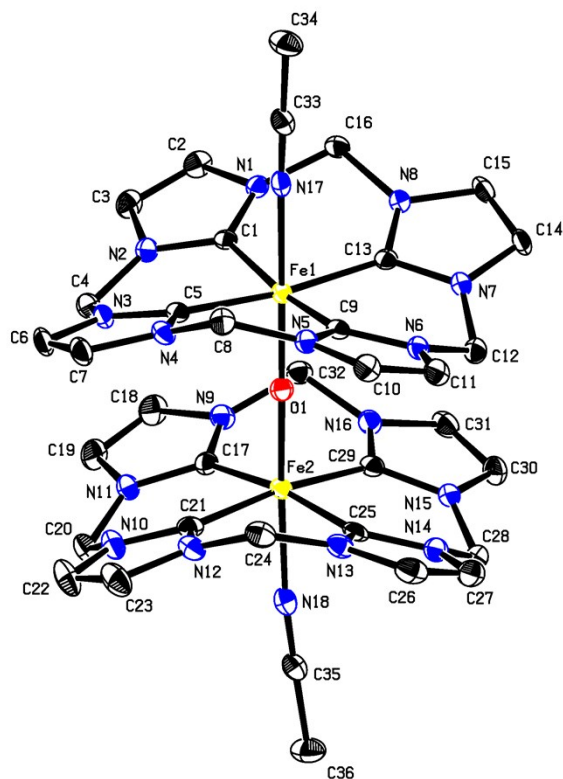


Fig. S1: ORTEP-style drawing of the cationic fragment of complex **3**. Hydrogen atoms, co-crystallized solvent molecules and five PF_6^- anions are omitted for clarity and thermal ellipsoids are shown at a 50% probability level.

Selected bond lengths (Å) and angles (°): Fe1–C1: 1.929(2), Fe1–C5: 1.924(3), Fe1–C9: 1.931(2), Fe1–C13: 1.939(3), Fe1–O1: 1.7272(17), Fe1–N17: 1.984(2), N17–C33: 1.138(3), Fe2–C17: 1.929(3), Fe2–C21: 1.931(3), Fe2–C25: 1.931(3), Fe2–C29: 1.929(3), Fe2–O1: 1.7298(17), Fe2–N18: 1.987(2), N18–C35: 1.141(3), C1–Fe1–C5: 91.72(9), C5–Fe1–C9: 90.29(10), C9–Fe1–C13: 89.52(10), C1–Fe1–C13: 89.63(10), O1–Fe1–N17: 178.09(8), C17–Fe2–C21: 89.96(11), C21–Fe2–C25: 89.01(11), C25–Fe2–C29: 90.39(11), C17–Fe2–C29: 89.29(11), O1–Fe2–N18: 177.18(9), Fe1–O1–Fe2: 176.34(11)

Single crystals of **3** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution at $-40\text{ }^\circ\text{C}$.

Tab. S1: Crystallographic data of complex **3**.

Substance identification	Complex
CCDC	2077633
Empirical formula	C ₄₂ H ₄₇ F ₃₀ Fe ₂ N ₂₁ OP ₅
Fw [g mol ⁻¹]	1689.55
T [K]	123(2)
Crystal system	triclinic
Space group	<i>P</i> -1
a [Å]	12.1708(3)
b [Å]	12.6323(3)
c [Å]	23.6169(5)
α [deg]	29.9980(10)
β [deg]	93.5180(10)
γ [deg]	115,2720(10)
V [Å ³]	3264.86(13)
Z	2
Density (calcd) [g cm ⁻³]	1.728
μ [mm ⁻¹]	0.706
F (000)	1702
Crystal size (mm ³)	0.16 × 0.27 × 0.33
θ range for data collection [deg]	1.98 to 25.41
Reflections collected	84113
Independent reflections	11929 [R(int)= 0.0405]
Data/restraints/parameters	11929 / 81 / 983
GOF on F ²	1.024
Final R1	R1 = 0.0558,
wR2 [I > 2σ(I)]	wR2 = 0.0868
Largest diff. peak and hole [eÅ ⁻³]	0.631 and -0.348

3. Experimental Data

Bis- μ_2 -oxo[calix[4]imidazol]iron(III)/(IV) hexafluorophosphate (3)

Bis- μ_2 -oxo[calix[4]imidazol]iron(III) hexafluorophosphate **2** (0.100 g, 0.074 mmol, 1 eq.)² was dissolved in 2 mL acetonitrile and cooled to -40 °C. An equimolar amount of thianthrenyl hexafluorophosphate (0.027 g, 0.074 mmol, 1 eq.) in acetonitrile was added. The burgundy solution was stirred for 15 minutes at -40 °C and precipitated with diethylether. After drying *in vacuo*, the product was obtained as burgundy powder (0.099 g, 0.063 mmol, 85%).

¹H-NMR (400 MHz, CD₃CN, 296 K): no signals observable.

Anal. Calcd. for C₃₆H₃₈F₃₀Fe₂N₁₈OP₅: C 27.45; H 2.43; N 16.00. Found: C 27.41; H 2.54; N 15.76.

4. UV/Vis-Spectra

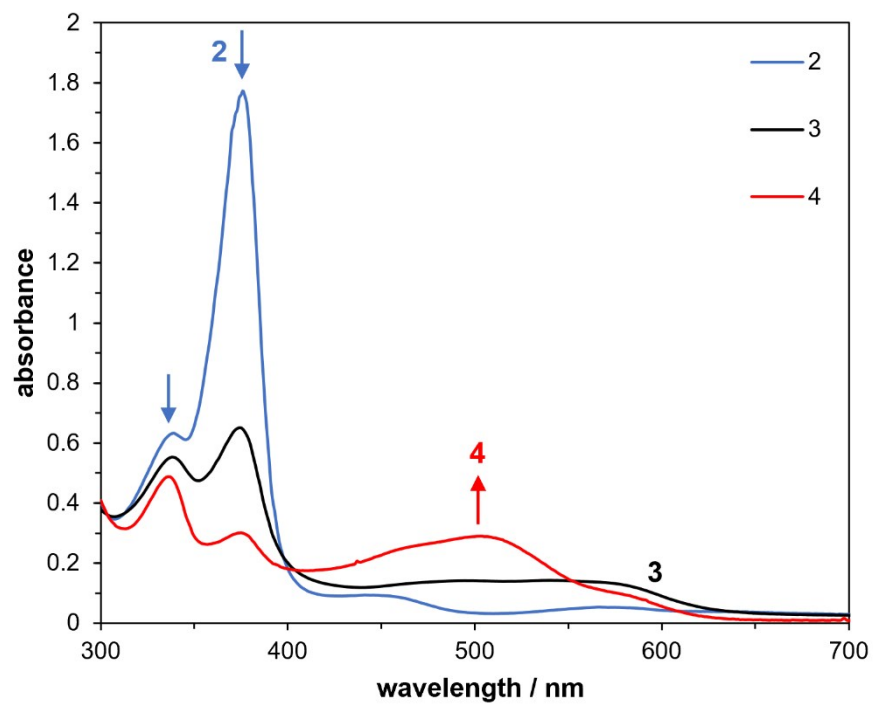
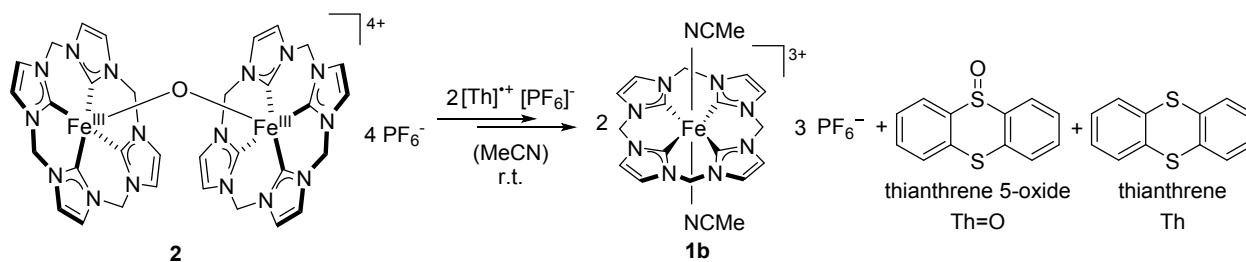


Fig. S2: UV/Vis spectrum of **2**, **3**, and **4**. $T = -40\text{ }^{\circ}\text{C}$, $c = 3.5 \cdot 10^{-4}\text{ M}$ in dry and degassed MeCN.

5. $^1\text{H-NMR}$ -spectra in the paramagnetic region



15 mg of diiron(III)-oxo complex **2** (0.011 mmol, 1 eq.) were dissolved in ~ 0.5 mL dry and degassed acetonitrile- d_3 in a dried *J-Young* NMR tube. After addition of thianthrenyl hexafluorophosphate (8 mg, 0.022 mmol, 2 eq.), the mixture was vigorously shaken resulting in an instantaneous color change from dark green (**2**) to reddish-purple indicating the formation of **1b**.

In the $^1\text{H-NMR}$ spectrum (Fig. S3) the signals of **1b** are located at 44.02 ppm and -11.50 ppm. The first is representing the CH_2 -bridge and the latter the CH -backbone of the imidazole units of the tetracarbenic ligand. They are both in a 1:1 ratio. The peaks fit well with a blank spectrum of **1b** taken at 293 K (Fig. S5). Fig. S6 furthermore shows the signals of **1b** at various temperatures from -40 $^\circ\text{C}$ to 50 $^\circ\text{C}$.

Fig. S4 depicts the area between 8.00 ppm and 6.90 ppm of Fig. S3; the signals of both $\text{Th}=\text{O}$ and Th are present. The signals of Th can be assigned to the peaks at 7.14 and 7.35 ppm, where the latter is overlapping with one signal of $\text{Th}=\text{O}$. The remaining $\text{Th}=\text{O}$ signals are at 7.65, 7.57 and 7.44 ppm. The integrals of $\text{Th}=\text{O}$ are very close to each other in a 1:1:1:1 ratio. The chemical shifts of both Th and $\text{Th}=\text{O}$ match well with those reported in the literature.^{5, 6}

$^1\text{H-NMR}$ (400 MHz, CD_3CN , 296 K): δ 44.02 (s, 16H, **1b**, CH_2), 7.65 (m, 2H, $\text{Th}=\text{O}$, CH), 7.57 (m, 2H, $\text{Th}=\text{O}$, CH), 7.44 (m, 2H, $\text{Th}=\text{O}$, CH), 7.35 (m, 6H, $\text{Th}=\text{O}$ (2H), Th (4H), CH), 7.14 (m, 4H, Th , CH), -11.50 (s, 16H, **1b**, CH).

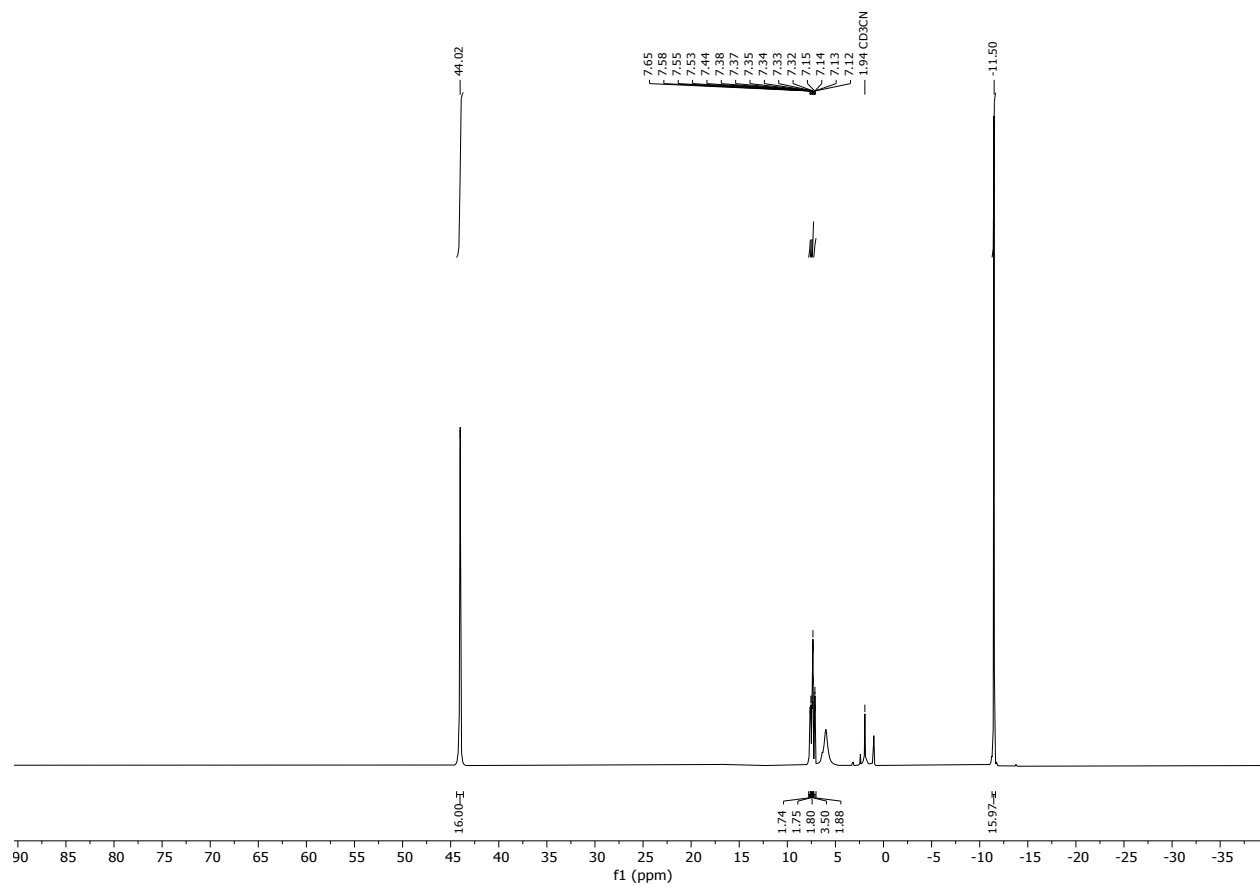


Fig. S3: $^1\text{H-NMR}$ spectrum of **1b**, **Th=O** and **Th** after addition of 2 eq. thianthrenyl hexafluorophosphate to a solution of **2**.

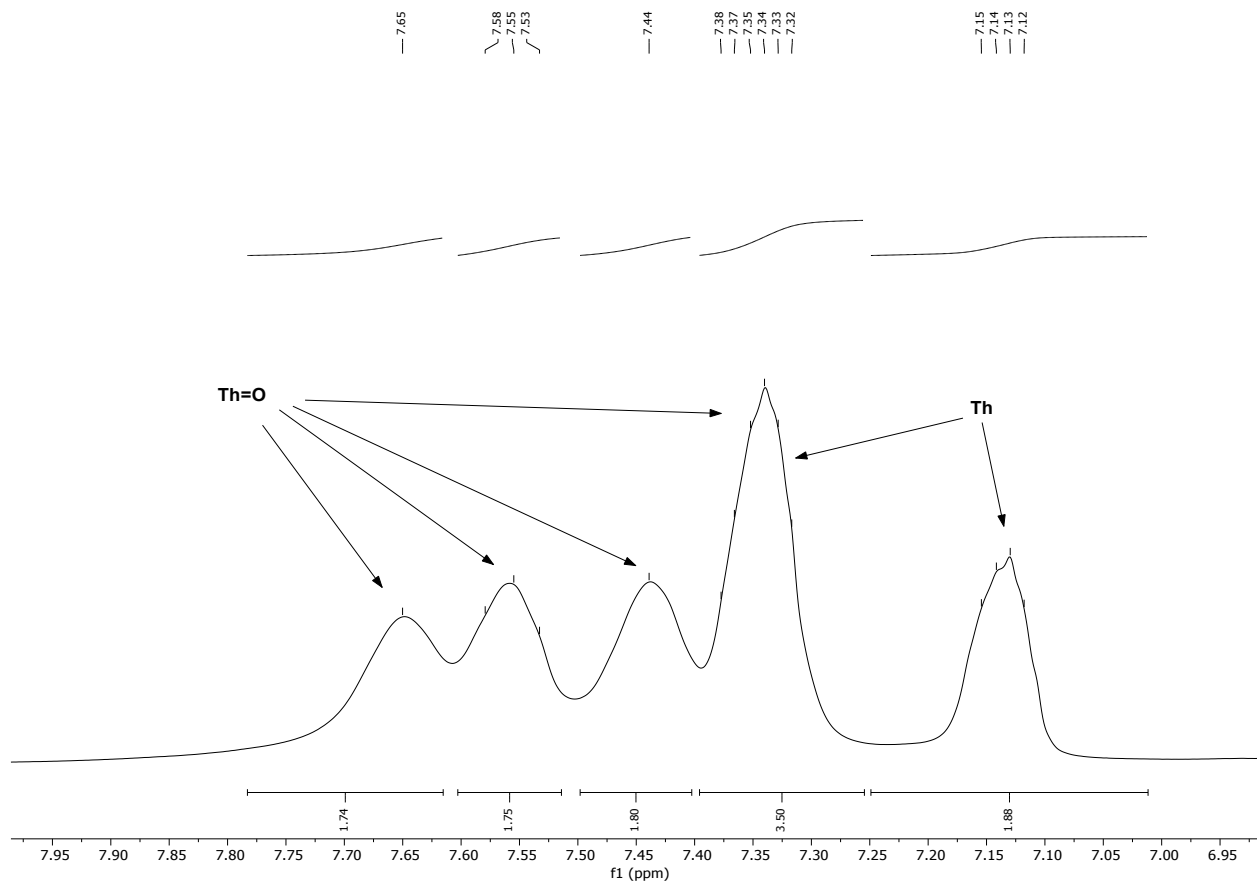


Fig. S4: Section from 8.00 to 6.90 ppm of Fig. S3.

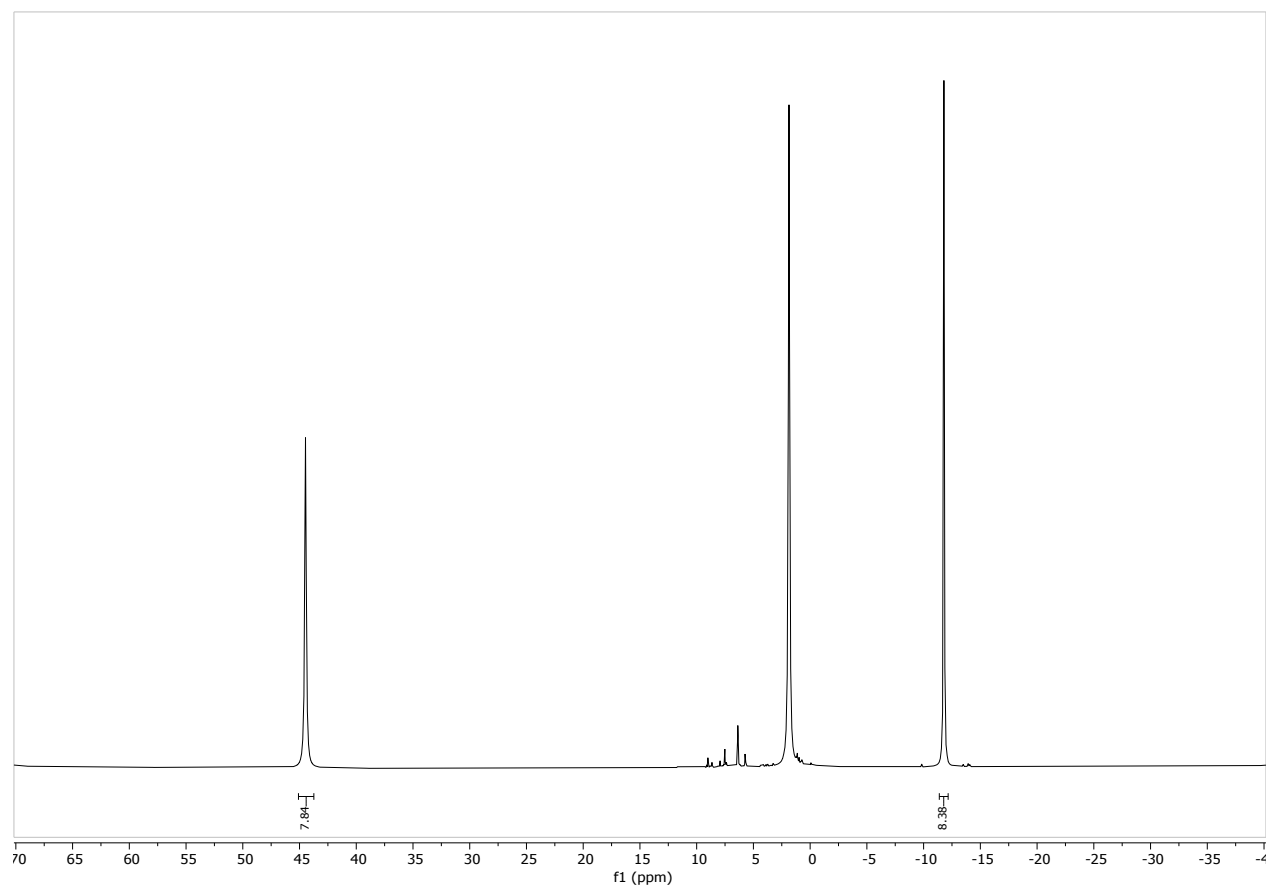


Fig. S5: ¹H-NMR spectrum of **1b** at 20 °C, 20 mg of **1b** in 0.5 mL in CD₃CN.

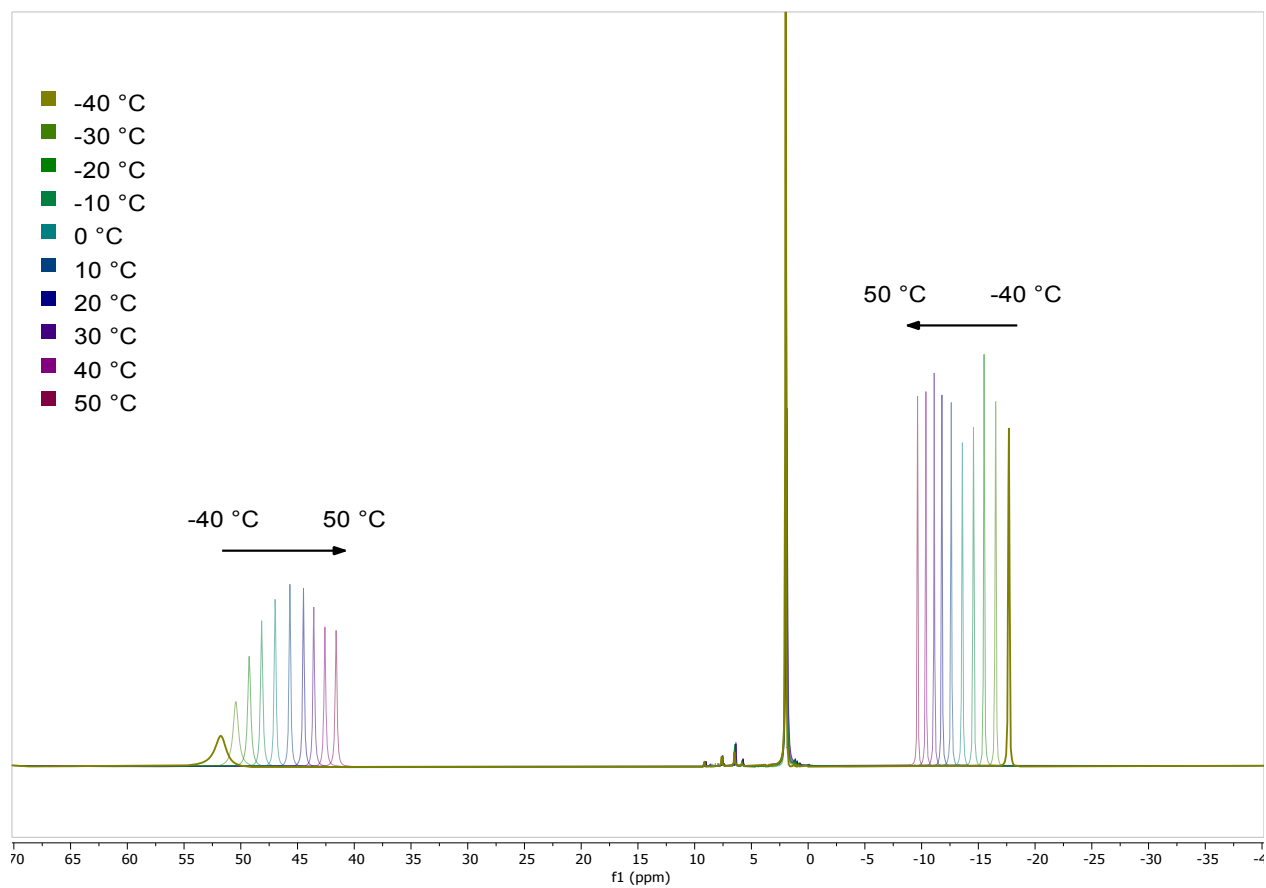


Fig. S6: Variable-temperature $^1\text{H-NMR}$ spectrum of **1b**. 20 mg of **1b** in 0.5 mL CD_3CN .

6. Evans' Method

The following formula were used to calculate the magnetic susceptibility X_m (neglecting the solvent correction term) and the magnetic moment μ , with Δf being the shift in frequency [Hz], f_0 the operating frequency of the NMR spectrometer [Hz], S_f the shape factor of the magnet ($S_f = (4\pi)/3$ due to cylindrical sample in superconducting magnet) and c with the concentration of the sample [mol/cm³].^{3, 4, 7, 8}

$$X_m = \frac{\Delta f}{f_0 S_f c}$$

$$\mu = \sqrt{8(X_m T)}$$

Tab. S2: Data of Evans-Method for **2** and **3**.

	2	3
f_0 [MHz]	400	400
m [mg]	10.4	14.7
M [g/mol]	1348.27	1575.34
m_{solvent} [g]	0.4	0.526
ρ [g/mL]	0.844	0.844
V [mL]	0.474	0.623
c [mol/mL]	$1.628 \cdot 10^{-5}$	$1.498 \cdot 10^{-5}$
T [K]	233.15	233.15
original solvent peak [ppm]	2.3	1.99
shifted solvent peak [ppm]	2.3	1.89
Δf [ppm]	0	0.1
Δf [Hz]	0	40
X_m [cm ³ /mol]	0	$159.388 \cdot 10^{-5}$
μ [μ B]	0	1.724

7. EPR Spectroscopy

X-band EPR spectra (approx. 9.27 GHz) were recorded at 173 K in a frozen solution of MeCN using a JEOL JES-FA 200 EPR spectrometer equipped with a variable temperature control unit ES-DVT4 and cooling with liquid nitrogen. The microwave frequency was measured via an Advantest R5372 microwave frequency counter. Measurements were performed with a modulation frequency of 0.4 mT, a receiver gain of 6·100 and a microwave power of 5 mW. The values for g and A were determined using a Mn^{2+} ($I = 5/2$) standard embedded in MgO. The fourth low field line is taken as reference signal set to $g = 1.981$. The measured EPR spectra were simulated using EasySpin 5.2.28⁹ and MatLab R2019b¹⁰ for determining the presented g and A values.

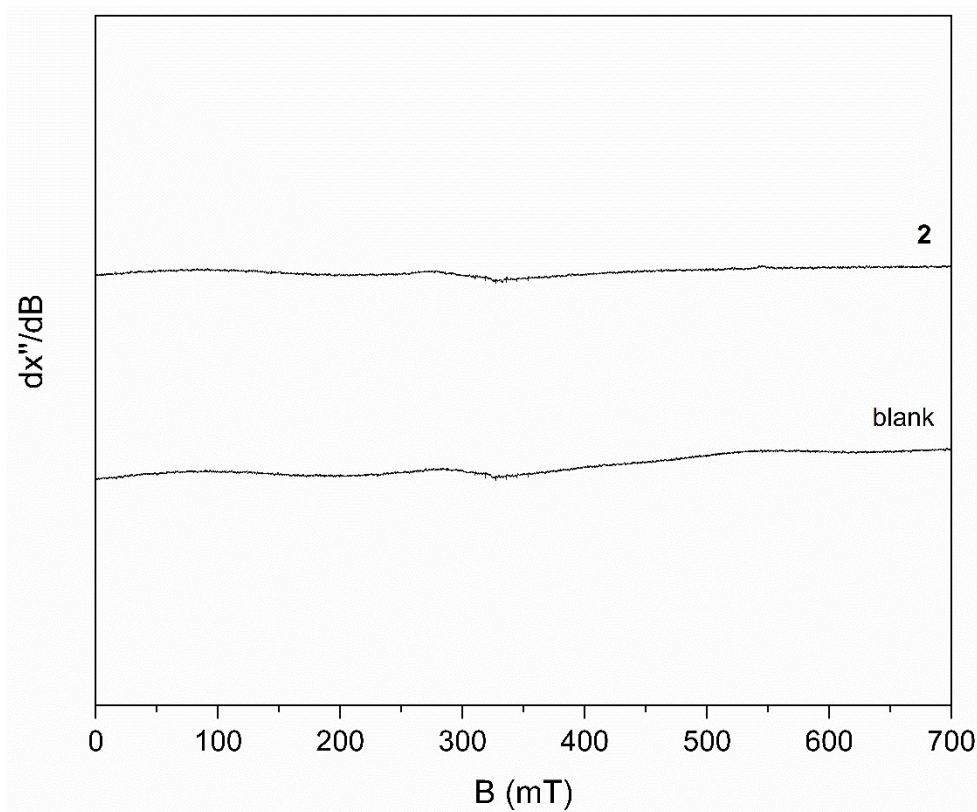


Fig. S7: EPR X-band spectra of complex **2** (top, 173 K, $4.6 \cdot 10^{-4}$ mol/L) and of the blank EPR tube (bottom, no solvent, 273 K). No signal observable.

Supplementary References:

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