

Supporting Information

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received. The following solvents were distilled and stored under argon: methanol, from $\text{Mg}(\text{OMe})_2$; tetrahydrofuran (THF), from sodium benzophenone ketyl.

Synthesis of L: To a solution of N-methylimidazole (20 mL, 0.25 mol) in anhydrous THF (250 mL) cooled to $-78\text{ }^\circ\text{C}$ was added dropwise a solution of n-BuLi (2.5M in hexane, 100 mL, 0.25 mol). After 30 min at $-78\text{ }^\circ\text{C}$ under argon, $\text{MeSCH}_2\text{CH}_2\text{CO}_2\text{Et}$ (12 mL, 83 mmol) was added dropwise to the yellow solution. The temperature was allowed to rise slowly to room temperature and maintained for 1 night. The mixture was extracted with EtOAc (3 x 200 mL) and the combined organic layers were washed with saturated aq. NaCl (2 x 100 mL), dried (MgSO_4), and evaporated under vacuum to dryness. The crude product was filtered over silica gel (5% MeOH/ CH_2Cl_2 as the eluant). The pale yellow solid obtained was crystallized from 1:1 EtOAc - cyclohexane to give L as colorless crystals (18.10 g, 82%). mp (from EtOAc - cyclohexane) $129\text{ }^\circ\text{C}$; ^1H NMR (250 MHz, CDCl_3): δ 6.92 (d, 2 H, $J = 1.1\text{ Hz}$, H_{im}), 6.77 (d, 2 H, H_{im}), 5.52 (s, 1 H, D_2O exchangeable, OH), 3.26 (s, 6 H, NMe), 2.74 (m, 2 H, CH_2), 2.50 (m, 2 H, CH_2), 2.06 (s, 3 H, SMe); ^{13}C NMR (63 MHz, CDCl_3): δ 147.1 ($\text{C}-2_{\text{im}}$), 125.9 + 123.5 ($\text{C}-4_{\text{im}}$ + $\text{C}-5_{\text{im}}$), 71.3 ($\text{C}-\text{OH}$), 33.3 (NCH_3), 28.6 (CH_2), 27.9 (CH_2), 15.6 (SCH_3); MS (CI, NH_3): 267 ($\text{M} + 1$); Elemental analysis: calcd for $\text{C}_{12}\text{H}_{18}\text{N}_4\text{OS}$ (266.36): C 54.11, H 6.81, N 21.03. Found: C 54.07, H 6.87, N 21.14.

$[\text{Fe}^{\text{II}}(\text{L})_2(\text{OH})](\text{BF}_4)$ (1): All experiments were carried out under Ar atmosphere. A solution of L (250 mg, 0.94 mmol) in degassed anhydrous MeOH (6 mL) was added dropwise to a solution of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (105 mg, 0.31 mmol) in degassed anhydrous MeOH (7 mL). The pale-yellow solution was stirred at room temperature for 1 h and evaporated under vacuum to dryness. The pale yellow oil was dissolved in anhydrous MeOH (5 mL) and the solution was kept in a glove box under slow diffusion of EtOAc vapor for *ca.* 1 months. Pale yellow crystals were collected and were used for single-crystal X-ray diffraction study (155 mg, 72%). Elemental analysis: calcd for $[\text{Fe}^{\text{II}}(\text{L})_2(\text{OH})](\text{BF}_4)$ ($\text{C}_{24}\text{H}_{37}\text{BF}_4\text{FeN}_8\text{O}_3\text{S}_2$, 692.39): C 41.63, H 5.39, N 16.18, S 9.26; found: C 41.31, H 4.98, N 16.01, S 8.92. UV/vis (DMF) [I_{max} nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 339 (2560), 296 (sh). electrospray MS (H_2O): m/z 587.1 $[\text{Fe}^{\text{II}}(\text{L})_2(\text{OH}) - \text{H}_2\text{O}]^+$.

[Fe^{III}(L)₂(OH)₂](BF₄) (2): A solution of L (1.023 g, 3.84 mmol) in anhydrous MeOH (10 mL) was added dropwise to a solution of Fe(BF₄)₂·6H₂O (433 mg, 1.28 mmol) in anhydrous MeOH (50 mL). The yellow solution was stirred at room temperature in the presence of air for 15 h and then evaporated under vacuum to dryness. The resulting yellow powder was dissolved in anhydrous MeOH (40 mL) and the solution was kept at room temperature for *ca.* 1 month. Yellow crystals were collected and were used for single-crystal X-ray diffraction study (318 mg, 35%). Elemental analysis: calcd for [Fe^{III}(L)₂(OH)₂](BF₄) (C₂₄H₃₈BF₄FeN₈O₄S₂, 709.39): C 40.64, H 5.40, N 15.80, S 9.04; found: C 40.27, H 5.31, N 15.59, S 8.73. UV/vis (DMF) (*I*_{max} nm): 341 (sh). electrospray MS (H₂O): *m/z* 586.7 [Fe^{III}(L)₂(OH)₂ - 2H₂O]⁺.

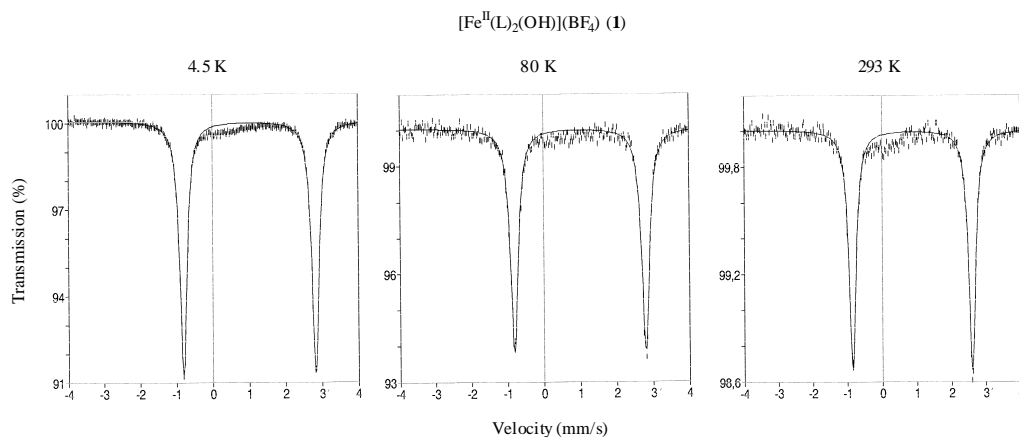
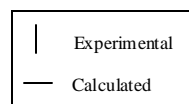
Physical Measurements

Melting points were determined with a Büchi SMP-20 apparatus and are uncorrected. ¹H NMR spectra were recorded with a Bruker AM-250 spectrometer, and chemical shifts refer to an internal standard of Me₄Si (*d* = 0.00). Mass spectra were recorded at Ecole Normale Supérieure, Paris. Elemental analyses were performed by Service de Microanalyse, I.C.S.N., Gif-sur-Yvette.

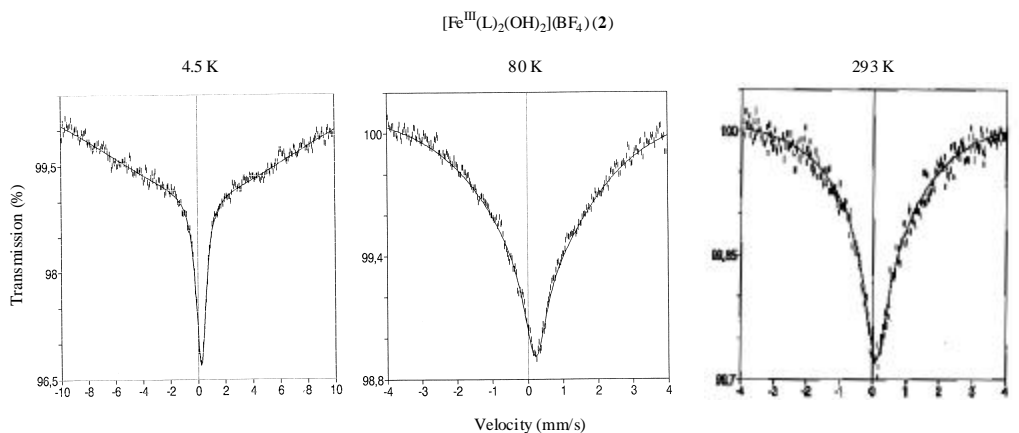
UV-visible spectra were recorded with an Uvikon 820 spectrophotometer. EPR spectra were obtained with a Bruker Elexsys 500 spectrometer equipped with a SHQ 001 cavity operating at X-band. The EPR measurements were performed at 10 K using an Oxford liquid helium continuous flow cryostat. Variable-temperature magnetic data were collected with a Quantum Design MPMS SQUID susceptometer in the 4–300 K temperature range.

Mössbauer measurements were obtained on a constant-acceleration conventional spectrometer with a 50 mCi source of ⁵⁷Co (Rh matrix). Isomer shift values (*δ*) are given with respect to metallic iron at room temperature. The absorber was a sample of 100 mg of microcrystalline powder enclosed in a 20 mm diameter cylindrical plastic sample-folder, the size of which had been determined to optimize the absorption. The spectra were obtained at 4, 80 K and 295 K by using a MD 306 Oxford cryostat monitored by an Oxford ITC4 servocontrol device (± 0.1 K accuracy). A least-squares computer program was used to fit the Mössbauer parameters and determine their standard deviations of statistical origin.¹

Mössbauer measurements (solid state)



1	4.5 K	80 K	293 K
$\delta(\text{mm.s}^{-1})$	1.084(1)	1.069(2)	0.956(2)
$\Delta E_Q(\text{mm.s}^{-1})$	3.506(2)	3.489(3)	3.333(3)



2	4.5 K	80 K	293 K
$\delta(\text{mm.s}^{-1})$	0.42(5)	0.44(2)	0.38(4)
$\Delta E_Q(\text{mm.s}^{-1})$	~ 0	~ 0	~ 0

Crystallographic Data Collection and Structural Determination

Crystal data were collected at 298 K on a Nonius CAD4 diffractometer, using a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The final unit cell parameters were obtained by least-squares refinement of the setting angles of 25 well-centered reflections. Two standard reflections per image were monitored periodically showing no significant fluctuations during data collection. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs)² were applied. A secondary extinction correction was unnecessary. The structure of **1** was solved by direct methods (SHELXS)³ and successive Fourier maps. Computations were performed by using the PC version of CRYSTALS.⁴ Full matrix least-squares refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors. Real and imaginary parts of anomalous dispersion were taken into account. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.⁵ All hydrogen atoms were located on difference Fourier maps; they were given an overall isotropic thermal parameter. Non hydrogen atoms were refined anisotropically. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviations being less than 0.1 and no significant features in the last Fourier-difference map. Drawings of the molecules were performed with the programs ORTEP⁶ with 50% of probability displacement ellipsoids for non-hydrogen atoms. Crystal data collection and refinement parameters are gathered in Table S1, and selected bond distances and angles in Table S2.

Table S1. Crystal Data Collection and Refinement Parameters for $[\text{Fe}^{\text{II}}(\text{L})_2(\text{OH})](\text{BF}_4)$ (**1**) and $[\text{Fe}^{\text{III}}(\text{L})_2(\text{OH})_2](\text{BF}_4)$ (**2**)

complex	$[\text{Fe}^{\text{II}}(\text{L})_2(\text{OH})](\text{BF}_4)$ (1)	$[\text{Fe}^{\text{III}}(\text{L})_2(\text{OH})_2](\text{BF}_4)$ (2)
formula	$\text{C}_{24}\text{H}_{37}\text{BF}_4\text{FeN}_8\text{O}_3\text{S}_2$	$\text{C}_{24}\text{H}_{87}\text{BF}_4\text{FeN}_8\text{O}_4\text{S}_2$
formula weight	692.38	709.39
color of crystal	pale yellow	yellow
a (Å)	11.819(3)	12.100(5)
b (Å)	12.073(4)	18.793(4)
c (Å)	12.685(2)	13.899(7)
α (°)	99.50(2)	90
β (°)	108.49(2)	103.19(2)
γ (°)	111.33(2)	90
V (Å ³)	1516.4(7)	3077(2)
Z	2	4
crystal system	triclinic	monoclinic
space group	P -1	P 2 ₁ /a
I (Å)	0.71073	0.71073
density ρ (g.cm ⁻³)	1.510	1.523
temperature (K)	293 (2)	293 (2)
GOF	1.183	1.075
$R = \Sigma F_o - F_c / \Sigma F_o $	0.0730	0.0662
R_w^*	0.1508	0.1496
$R_w^* = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$		

Table S2. Selected Bond Distances (Å) and Angles (°) for $[\text{Fe}^{\text{II}}(\text{L})_2(\text{OH})](\text{BF}_4)$ (**1**) and $[\text{Fe}^{\text{III}}(\text{L})_2(\text{OH})_2](\text{BF}_4)$ (**2**)

	$[\text{Fe}^{\text{II}}(\text{L})_2(\text{OH})]^+$ (1)	$[\text{Fe}^{\text{III}}(\text{L})_2(\text{OH})_2]^+$ (2)
Fe1–O1	1.938(3)	1.888(3)
Fe1–O2	—	1.882(4)
Fe1–N11	2.150(5)	2.120(5)
Fe1–N21	2.105(5)	2.128(5)
Fe1–N31	2.116(5)	2.114(5)
Fe1–N41	2.130(5)	2.096(5)
O1–Fe–O2	—	89.43(17)
O1–Fe1–N11	88.53(17)	95.15(18)
O1–Fe1–N21	121.01(17)	85.81(17)
O1–Fe1–N31	125.90(17)	170.14(18)
O1–Fe1–N41	91.26(18)	88.97(18)
O2–Fe1–N11	—	88.41(18)
O2–Fe1–N21	—	168.58(18)
O2–Fe1–N31	—	87.58(17)
O2–Fe1–N41	—	97.25(18)
N11–Fe1–N21	82.49(19)	81.70(19)
N11–Fe1–N31	96.55(19)	94.2(2)
N11–Fe–N41	179.3(2)	173.0(2)
N21–Fe–N31	113.04(18)	98.76(19)
N21–Fe–N41	98.22(19)	93.04(19)
N31–Fe–N41	83.00(19)	82.09(19)

References

- (1) Varret, F. *Proceedings of the International Conference on Mössbauer Effect Applications*; Jaipur, India 1981; Indian National Science Academy: New Delhi 1982.
- (2) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A39, 158-166.
- (3) Sheldrick, G. M. *SHELXS: Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.
- (4) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *Crystals User Guide*; Chemical Crystallography Laboratory: Oxford, U.K., 1988.

- (5) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.
- (6) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565-565.